Vol. II

TRANSCRIPT OF RECORD

Supreme Court of the United States

OCTOBER TERM, 1927

No. 182

CORONA CORD TIRE COMPANY, PETITIONER,

vs.

DOVAN CHEMICAL CORPORATION

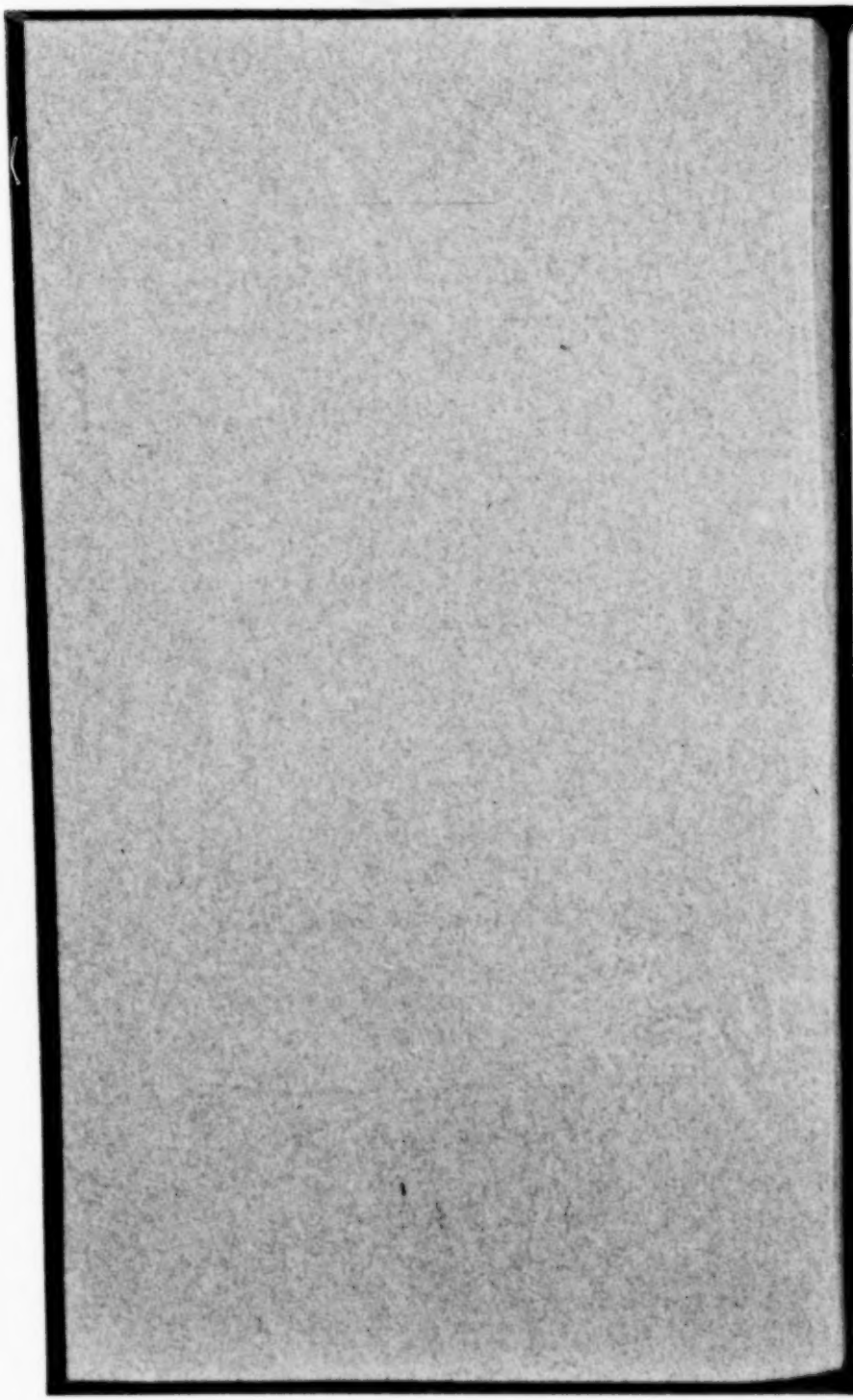
ON WRIT OF CERTIORARI TO THE UNITED STATES CIRCUIT COURT OF APPEALS FOR THE THIRD CIRCUIT

M1.230 888. 823 c

PETITION FOR CERTIORARI FILED FEBRUARY 21, 1927

CERTIORARI GRANTED APRIL 11, 1927

(32,482)



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VOLUME II

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JUDD & DETWEILER (INC.), PRINTERS, WASHINGTON, D. C., SEPTEMBER 16, 1927

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UNITED STATES PATENT OFFICE.

MORRIS L. WEISS, OF BROOKLYN, NEW YORK, ASSIGNOR TO DOVAN CHEMICAL CORPORATION, OF WILMINGTON, DELAWARE, A CORPORATION OF DELAWARE.

VULCANIZATION ACCELERATOR.

1,411,231. Specification of Letters Patent. Patented Mar. 28, 1922.

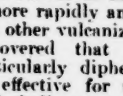
No Drawing. Application filed November 12, 1921. Serial No. 514,727

To all whom it may concern:

Be it known that I, MORRIS L. WEISS, a citizen of the United States, residing in the borough of Brooklyn, county of Kings, city and State of New York, have invented certain new and useful Improvements in Vulcanization Accelerators, of which the following is a full, clear, concise, and exact description.

The object of my invention is to improve rubber compounds so that the finished product shall be of superior quality and so that the time required for vulcanization shall be greatly reduced over that ordinarily required for such purpose. It is known that when certain organic substances are added to the rubber mix during the compounding, a catalytic or similar action is produced which causes the rubber or similar gum to unite or react more rapidly and thoroughly with sulphur or other vulcanizing agents.

I have discovered that disubstituted guanidines particularly diphenylguanidine are particularly effective for this purpose. This substance is indicated by the formula



I am aware that disubstituted guanidines have been produced by laboratory methods and have been known to chemists for many years beginning about the year 1848 with the work of A. W. Hoffman (An. Chem. Pharm. 67–129), but down to time of my researches in accelerators of this type, it was apparently not known that di-substituted guanidines were efficacious or useful as accelerators in vulcanizing, nor that this substance could be produced in sufficiently large quantities in a substantially pure form, or at a sufficiently low cost to be available for this purpose.

I am aware that triphenylguanidine has been suggested, and probably used to some extent, as an accelerator in the vulcanization of rubber, but the use of diphenylguanidine for that purpose appears to have been unknown prior to my researches on this substance.

I have found that diphenylguanidine is much more powerful and efficacious as an accelerator in vulcanization than triphenylguanidine. For example, in the vulcanization of hard rubber articles the use of diphenylguanidine not only hastens the vulcanizating action but results in a final product much superior in texture, strength, durability and aging qualities over that when the triphenylguanidine is used. A greatly improved product also results when diphenylguanidine is used as an accelerator in the vulcanization of soft rubber compounds, particularly as regards elasticity, aging qualities and freedom from "bloom." In these and similar instances, it has been found that the use of triphenylguanidine requires from two to three times as long a period in vulcanizing as when diphenylguanidine is used, particularly at lower heat or steam pressures than those commonly employed.

In my prior application Serial No. 482,143 filed July 2, 1921, I have described and claimed a process for producing and purifying diphenylguanidine in commercial quantities, and have therein given a résumé of the historical development of the methods of producing the same.

As set forth in said application, I, at present, prefer to produce my improved accelerator by desulphurizing thiocarbanilide by the action of a metallic oxide, such as lead oxide, zinc oxide, etc., in an alcoholic solution of an ammonium salt, such as ammonium nitrate.

The present patent application therefore relates to the vulcanization of rubber or similar substances, in which disubstituted guanidines are employed as the accelerating agent or catalyzer, and particularly diphenylguanidine.

The method of carrying out my invention, which I at present deem preferable, may be illustrated by the following example:

The rubber may be compounded in the following proportions: 50 parts by weight of new rubber, 45.5 parts by weight of zinc oxide, 3.5 parts by weight of sulphur, 1 part by weight of diphenylguanidine.

These are mixed together in any suitable way, such as by milling, and then vulcanized or cured in the usual molds or otherwise under heat corresponding to a steam pressure of about 40 lbs. per square inch. This vulcanizing temperature should be continued until the compound is suitably vulcanized, which requires from 10 to 20

Plaintiff's Exhibit No. 1

1

minutes depending upon the shape and size of the articles being vulcanized.

It will therefore be appreciated that when using the accelerator according to my invention the vulcanization is accomplished by using comparatively small quantities of the accelerator, thereby obviating undesirable loading or adulteration of the rubber compound. Furthermore, by the use of such accelerator, the texture and durability of the final product is greatly improved and the tendency commonly present in vulcanized rubber to bloom and become brittle with age is greatly reduced if not entirely obviated. My improved accelerator is particularly useful and valuable where it is desired to produce a harder or less elastic portion in an article leaving other parts which are required to be more elastic and flexible, such as in automobile tires where the beadstock is usually made harder than the body or carcass of the tire proper. The relative amounts of vulcanizing agent and accelerator may be so proportioned that the various parts of a single article may be cured to different degrees of hardness without danger of over-curing the softer or more elastic parts. I have found moreover that diphenylguanidine does not need zinc oxide to shorten the time of cure. I however prefer to use zinc oxide on account of its effects on the physical properties of the product.

Having thus described this example of my invention and the method of using the same, I do not wish to be understood as being limited to the exact proportions, ingredients, temperatures, etc., indicated, for various changes may be made without departing from the essential features of my invention as set forth in the accompanying claims.

What I claim and desire to protect by Letters Patent is:

1. The process of treating rubber or similar materials, which comprises combining with the rubber compound a di-substituted guanidine.

2. The process of treating rubber or similar materials which comprises combining with rubber compound a di-substituted guanidine comprising two phenyl radicles or groups.

3. The process of treating rubber or similar materials which comprises combining with the rubber compound an accelerator derived from thiocarbanilide in which the sulphur is substituted by an imide group.

4. The process of treating rubber or similar materials which comprises combining with the rubber compound diphenylguanidine.

5. The process of treating rubber or similar materials which comprises combining with the rubber compound a vulcanizing agent and a di-substituted guanidine accelerator.

6. The process of treating rubber or similar materials which comprises combining with the rubber compound a vulcanizing agent and a di-substituted guanidine comprising two phenyl radicles or groups.

7. The process of treating rubber or similar materials which comprises combining with the rubber compound a vulcanizing agent and an accelerator derived from thiocarbanilide in which the sulphur is substituted by an imide group.

8. The process of treating rubber or similar materials, which comprises combining with the rubber compound a vulcanizing agent and diphenylguanidine.

9. A vulcanizing compound of rubber or similar material combined with a vulcanizing agent and a di-substituted guanidine.

10. A vulcanized compound of rubber or similar material combined with a vulcanizing agent and di-substituted guanidine comprising two phenyl radicles or groups.

11. A vulcanized compound of rubber or similar material combined with a vulcanizing agent and an accelerator derived from thiocarbanilide in which the sulphur is substituted by an imide group.

12. A vulcanized compound of rubber or similar material combined with a vulcanizing agent and diphenylguanidine.

Signed at New York, N. Y., November 10th, 1921.

MORRIS L. WEISS.

PLAINTIFF'S EXHIBIT No. 4

Memorandum of agreement made this thirteenth day of April between M. L. Weiss of New York City, party of the first part, and Van Lear Woodward of New Brighton, N. Y., and H. S. Doty of Passaic, N. J., parties of the second part.

In consideration of a salary of * * * dollars (* * *) per month, to be paid the party of the first part by the parties of the second part, commencing April 15, 1920, said party of the first part agrees to make and produce, in quarters and with equipment supplied by the parties of the second part, a certain chemical known as Diphenylguanidine, of a quality similar to sample handed the parties of the second part by the party of the first part and labeled A-April 13, 1920, which material is to be used as an accelerator by the rubber industry.

Parties of the second part agree to use their best endeavors to properly put this commodity on the market.

Parties of the second part further agree to pay to the party of the first part the sum of * * * cents (* * *) per pound on all of this material sold.

Party of the first part agrees to deposit with the parties of the second part, and receipt of same is hereby acknowledged, the formula and process for the manufacture of said Diphenylguanidine, as a protection to the parties of the second part in return for their providing the party of the first part with the equipment to produce.

Party of the first part agrees to give the parties of the second part first option upon any other chemicals that he can now or hereafter produce on a royalty basis to be arranged at that time.

Party of the first part agrees that the parties of the second part may at their option at any time during the life of this agreement, or any renewals thereto, form a corporation to produce, manufacture and sell said Diphenylguanidine, provided said corporation carriers out all the clauses of this agreement.

This agreement to be in force for a period of six months from date and to be automatically renewed for like periods

of six months, unless either party advises the other party in writing thirty days previous to the expiration of this agreement, or any renewals thereto, his or their intention not to renew.

In witness whereto said parties have hereunto set their hands and seals executing this agreement in triplicate this thirteenth day of April, 1920.

M. L. Weiss, Van Lear Woodward, H. S. Doty.

Witness: J. H. McCoy, H. W. Loving, Addison H. Brown.

#0

MYE

Packer

Bl. Lieps	15
Batanga	40
Mam	11
Lane	2
Ind	3
Zane	24½
Crowte	4 (Diffends 1)
Quertes	½
	100

Plf's Exhibit No. 5
Mye Formula
Oct 9/25
Pack.

cure 30/35
clong 14½
Tenale 25 30
set ½

#6 NUMBER X 1764 MADE FOR Imited Norwalk Tire P. O.

		A	B	C	D	E	F	G	H
S. Sheets	79	70	70	79	87½				
Coarse									
Canelle									
Guayule									
Methe	15	15	10						
Zinger		8½	13	13					
A									
B									
C									
D									
F									
G									
Difficile (Pine)					¾				
Al Flake									
Lime									
Litharge									
Sulphur	3	3½	4	4	3½				
White Lead									
Zinc	3	3	3	2					
Magnesia Metric				2	1 7½				
Total	100	100	100	100					
Sp. Grav. Cost and Prices	Floats 68.47 1.60 54.9	5191 1.60 53.41	5191 1.60 5791						
	Glenn Rub	Glenn Rub	Glenn Rub						
Cure	65/754	67/754	65/754	67/754					
Stretch									
Strength									
Set									
Color									
Date	7/8/19	7/16/19	7/16/19	8/6/19	7/20/19				

Remarks Norwalk Tests: Nr 20-14 c Sens. 2670-2630 = Set ¼-3/16

Plaintiff's Exhibit No. 7

3

723

NUMBER X 1773 MADE FOR Red Tube P O _____

		A	B	C	D	E	F	G	H
Sheets	91½	91	90½	90					
A									
B									
C									
D									
F									
G									
		½	3/8	3/4					
Plate									
	2½	2½	2½	3½					
Land									
	2	2	4¼	4¼					
Rod	2	2							
	2	2	2	4½					
			2	81					
			139/192						
			18						
			1460						
			18						
	Paid →		→	→					
	11-1-19 →		12-5-19	12-11-19					

Plaintiff's Exhibti No. 8

721

NUMBER X #3 1777 MADE FOR Inner Tube Spring Cement P O _____

		A	B	C	D	E	F	G	H
S. Sheets									
Coarse									
Caucho									
Guayule									
55	60								
A									
B									
C									
D									
P									
U									
Difdy Gum	10 1/4								
Al Flake									
Lime									
Litharge									
Sulphur	1								
White Lead									
Zinc	11								
Coloring	17								
Carb Bis	1/4								
Total									
Sp. Grav. Cost and Prices									
Cure									
Stretch									
Strength									
Set									
Color									
Date									
Remarks									

7

Plaintiff's Exhibit No. 9

COPY BOUND CLOS

Plaintiff's Exhibit No. 10.

("X" Book pages X 2000 to X 2074)
Including an enlargement of a portion of page 2034

IN CENTER

NUMBER X 2210 MADE FOR Action of organic accelerators P. O.

		A	B	C	D	E	F	G	H
S. Sulfur	50	50	50	50	50	50	50	50	
Cumar									
Cumbo									
Captax							E		
Cumate							2		
A									
B									
C									
D									
F									
G									
Al Flake									
Lime									
Litharge									
Sulphur	3	3	3	3	3	3	3	3	
White Lead									
Zinc	47	47	47	47	47	47	47	47	
Aniline Oil		2							
4-Dimethylaniline			1					½	
Diphenylguanidine				2				1½	
Diphenylamine					1				
Naphthylamine						1			
Total	100.00	102.00	101.00	102.00	101.00	101.00	102.00	102.00	
Sp. Grav. Cure and Press									
Cure									
Stretch									
Strength									
Set									
Color									
Date									
Remarks									

NUMBER X MADE FOR P O

		A	B	C	D	E	F	G	H
Cure . .	35/40	34/40	40/40	40/40	40/40	40/40	40/40		
2"h.t. .	15½	15	14½	15	15	15½	15		
T. St. . .	1350	3020	3230	3400	1170	2095	2100		
Set . .	5/16	3/16	3/8	7/16	5/16	1/4	5/16		
Cure . .	120/40	105/40	69/40	54/40	120/40	120/40	48/40		
2"h.t. .	15	14	14½	15½	15	15	13¾		
T. St. . .	1900	2148	2185	3340	2190	2635	2215		
Set . . .	1/4	5/16	5/16	1/2	1/4	3/8	1/4		
Cure . . .	129/40		99/40	49/40					
2"h.t. .	14¾		14	15					
T. St. . .	2135		2140	3265					
Set . . .	1/4		1/4	1/2					
Cure . . .	109/40								
2"h.t. .	14¾								
T. St. . .	2135								
Set . . .	5/16								

Remarks -

I 2000 - Standard Compound. O.K.

I 2000 B - Nitrosodimethylaniline HCl - From Rohland Anilines Co - Chicago Ill.
Yellow crystalline powder when fresh but deliquesces to black mush in air. Colors everything it comes in contact with yellow. Both Sym and Unsym are compounded. After cure blooms out yellow. After 3 days standing on batch accelerator properties seemed to have practically gone. When fresh, is a fairly good accelerator. Not practical for works.

I 2000 A - Aniline oil (pure) Too fast scorching powder.

I 2000 C - Diphenylguanidine - Very good accelerator. For making see Gattermann Pg 205 also Met. and Chem Engineering. Sept 15'16.

I 2000 D - Diphenylamine -

I 2000 E - Naphthylamine -

I 2000 F - Cumate

NUMBER X 2001 MADE FOR ACTION OF ORGANIC ACCELERATORS P. O. _____

		A	B	C	D	E	F	G	H
S. Sheets	50	50	50	50	50	60	60	60	
Coarse									
Cumar									
Gumyale									
Nitronaphalene						1			
Hexamethylenetetramine							1		
$C_6H_5NCH_2$								1	
A									
B									
C									
D									
F									
G									
Al Flake									
Lime									
Litharge									
Sulphur	3	3	3	3	3	3	3	3	
White Lead	47	47	47	47	47	47	47	47	
Zinc									
Salicylic Acid	1/2								
Guanidine		1.	2						
Phenylhydrazine				1					
Phenylenediamine					1				
Aldehyde Ammonia			1/2						
Total	100.5	101.00	101.50	101.00	101.00	101.00	101.00	101.00	
Sp. Grav. Cost and Price									
Cure									
Stretch									
Strength									
Set									
Color									
Date									
Remarks									

NUMBER X _____ MADE FOR _____ P. O. _____

		A	B	C	D	E	F	G	H
Cure	40/40	40/40	59/40	Sponge	40/40	40/40	39/40	39/40	
2"h.@	15"	15"	13 1/4		No	Accel.	14	15	
T.St.	2115	2115	3150		Acceleration	Noted	3230	3510	
Set	3/16	3/16	5/16				7/16	1/4	
Cure	75/40	75/40	129/40				75/40	69/40	
2"h.@	14 1/2	14 1/2	13				13 1/2	15 1/2	
T.St.	3160	3160	2720				3580	3240	
Set	7/16	7/16	7/16				9/16	1/4	
Cure	129/40	129/40					59/40		
2"h.@	19 3/4	19 3/4					19		
T.St.	2165	2165					3181		
Set	1/2	1/2					3/4		
Cure							49/40		
2"h.@							19 1/2		
T.St.							2125		
Set							1/4		
Cure							59/40		
2"h.@							15 1/2		
T.St.							2690		
Set							5/16		
Cure							69/40		
2"h.@							15		
T.St.							2990		
Set							3/8		
Cure							79/40		
2"h.@							14 1/2		
T.St.							3130		
Set							3/8		

REMARKS:-

X2001 - NO ACCELERATION

X2001A - QUINOLINE - LIQUID BOILING AT 240 - SOME ACCELERATION.

X2001B - ALDEHYDE AMMONIA — YELLOW CRYS. POWDER - ODER STRONG OF NH_3. ACCELERATION VERY GOOD.

X2001C - PHENYLHYDROZINE - N.G.

X2001D - PHENYLENE DIAMINE - NO ACCELERATION -

X2001E - NITRONAPHALENE - " " "

X2001F - HEXAMETHYLENE TETRAMINE - NOT QUITE AS GOOD AS X2000E - DOES NOT ACCEL. IN SHIDDY -

X2001G - $C_6H_5NCH_2$ - PRODUCT OF ANILINE + FORMALDEHYDE - N.G.

NUMBER X 2002 MADE FOR ACTION OF ORGANIC ACCELERATORS P.O.

		A	B	C	D	E	F	G	H
R. Sheets	50	50							
Coarse									
Caucho									
Guayule									
Product A	1								
DINITROBENZOL		2		6	3	3		3	
						50			
A									
B									
C									93
D									
F				97	97		87	88	
G						44			
W									
Al Flake									
Lime							1	1	1
Litharge		10			3	3	9	8	9
Sulphur	3						4		2
White Lead									
Zinc	47	88							
Total	101.00	100.00		103	103	100	100	100	100
Sp. Grav. Cost and Prices									
Cure		60/70							30/40
Stretch		FAIR CURE		Test runs on shoulders - Dinitrobenzol unsatisfactory					11
Strength				S. in curing. Results showed this rate relcatively					100
Set				about the same as S. - No advantage over					3/8
Color				S. as far as physical properties.					Bl.
Date									3/17-17

Remarks "D" in A2002H treated with 5% Beta Naphthol and heated 4 hrs at 30 lbs in heater.
"D" used in A2002H1 same as in A2002H but washed with hot H_2O.

NUMBER X MADE FOR P O

		A	B	C	D	E	F	G	H
R. Sheets	60/40								
Coarse	15/4								
Caucho	3025								
Guayule	75								
	70/40								
	15 3/4								
	2500								
A	5/16								
B									
C									
D									
F									
G									
Al Flake									
Lime									
Litharge									
Sulphur									
White Lead									
Zinc									
Total									
Sp. Grav. Cost and Prices									
Cure									
Stretch									
Strength									
Set									
Color									
Date									

Remarks

NUMBER X 2003 MADE FOR ORGANIC ACCELERATION P. O.

		A	B	C	D	E	F	G	H
S. Sheets	60	50	60	50	50	10	10	60	50
Coarse									
Caucho									
Guayule									
DINITRONAPHTHALENE	1								
DINITROBENZOL		2							
BENZIDINE			1						
A									
B									
C									
D						57	57		
F									
G									
PICRIC PHENOL				1					
BETA NAPHTHOL					1				
P. PHENYL						1		1	
CROMITE							1		1
Al Flake									
Lime									
Litharge	10	10				10	10	10	10
Sulpher			3	3	3	2	2	3	3
White Lead									
Zinc	38	38	47	47	47	20	20	37	37
Total	100	100	101.00	101.00	101.00	100	20 0	101.00	101.00
Sp. Grav. Cost and Prices						Lampamin	P. Phenyl Chromite	Lampamin	P. Phenyl Chromite
Cure	64/100 to 120/140	80/10	64/40	60/40	64/40				
Stretch	No Cure	Fair Cure	Soft →	Way	Lampamin to 120/40				
Strength		But Test	Undercured	Undercured	very Undercured				
Set		Way Down	No Accln.	No Accln.	N.B.				
Color									
Date			2/9-17	2/8/17	2/14-17				
Remarks									

NUMBER X MADE FOR P. O.

	A	B	C	D	E	F	G	H
S. Sheets					39/40	39/40	49/40	49/40
Coarse					10 3/4	11	11 1/2	15 1/2
Caucho					860	650	3020	3920
Guayule					1/4	5/8	7/16	7/16
					37/40	39/40	57/40	59/40
					7 3/4	10	14 3/4	15
					675	685	2560	3035
A					1/5	1/5	3/8	1/2
B					49/40	49/40	60/40	60/40
C					10 1/4	12 1/2	14	15
D					775	770	2540	2965
F					1/4	7/16	7/16	7/16
G								
Al Flake								
Lime								
Litharge								
Sulpher								
White Lead								
Zinc								
Total								
Sp. Grav. Cost and Prices								
Cure								
Stretch								
Strength								
Set								
Color								
Date								
Remarks								

X 2004 MADE FOR ACTION OF ORGANIC ACCELERATORS (See X2002) SHOODY P O.

		A	B	C	D	E	F	G	H
				50					
Coarse									
Cascho									
Guayule									
Br. Crepe	4	4			4	4			
A									
B									
C									
D	60	60			60	60			
F									
G									
Br. Blk. Treads	15	15			15	15			
M.R.X.	4	4			4	4			
Inertia	4	4							
Al Flake									
Lime	1 1/2	1 1/2			1.5	1.5			
Litharge					5	7.			
Sulphur	1 1/2	1 1/2		3	1.5	1.5			
White Lead									
Zinc				47					
Fossil Flour	7	10			7.	7.			
P. Phenyl C_6H_5	3				2.				
Total	100	100			100	100			
Sp. Grav. Cost and Press									
	NEEL	NEEL			SAA X1	SAA X1			
Cure	30/75	30/75			30/40	30/40			
Stretch	POROUS				8 1/4	8 1/2			
Strength	X2004 Cured O.K.				625	605			
Set	X2004A Cured O.K.				1/4	1/4			
Color	Little difference in tire stock as to cure								
Date					3-23-42	3-23-42			

Remarks

Remarks of X2001 CHP

NUMBER X MADE FOR P O (10)

		A	B	C	D	E	F	G	H
S. Sheets					20/30	30/30			
Coarse					8 1/4	8			
Cascho					570	610			
Guayule					1/4	1/4			
					29/30	30/30			
					8 1/4	8			
					570	646			
A					5/6	1/4			
B									
C									
D									
F									
G									
Al Flake									
Lime									
Litharge									
Sulphur									
White Lead									
Zinc									
Total									
Sp. Grav. Cost and Prices									
Cure									
Stretch									
Strength									
Set									
Color									
Date									

Remarks

NUMBER X 2005 MADE FOR Action Of Organic Accel. P. O. on Shoddies

	(2004C)	A	B	C	D	E	F	G	H	I
S. Sheets	60									
Cotton										
Canvas										
Oxygrain										
Dynamyl Guanidine	1									
D. Shoddy		93	93			93				
Z. Shoddy				93	93		93			
C Shoddy								70	70	70
anilyldiphenyl guanidine		1		1	-					
Diphenyl Guanidine			1		1			3		
Br. Crepe								5	5	5
Al Flake										
Lime		1	1	1	1	1	1	1	1	1
Litharge		1	1	1	1	2	2			
Sulphur	3	4	4	4	4	4	4	4	4	4
White Lead										
Zinc	47							~~17~~		
Barytes								17	20	18
Phenyl-beta-naphthylamine										2
Total	~101.00	100	100	100	100	100	100	100	100	100
Sp. Grav. Cost and Prices										
Cure	144/40	34/40	40/40	34/40	30/40	34/40	34/40	34/40	28/35	35/35	42/30
Stretch	N.G.	7	7/4	7/4	7	7	6 1/2	6	6 1/4	7 1/2	11	11 1/4	9 1/2
Strength		360	380	380	380	340	345	395	395	390	430	510	528	618	690
Set		3/32	4/32	3/32	3/32	4/32	5/32	5/32	7/16	4/32	9/32	9/32	13/32	4/4	9/4
Color															
Date	4/22	6-13-18	6-13-18	6-13-18	6-13-18	6-13-18	6-13-18	6-13-18	6-13-18	2-21-19	2-21-19	2-21-19
Remarks										Less set, stretch, cure	Stretch, set	

NUMBER X 2006 MADE FOR action of Organic accel. on Shoddies P. O.

	A	B	C	D	E	F	G	H
S. Sheets								
Cotton								
Canvas								
Oxygrain								
C. Shoddy	93	93	93	95.5	95	93	98	70
Cromite		3						
Diphenylguanidine								
Br. Crepe		3						5
B								
C								
D								
F								
G								
anilyldiphenylguanidine			3					
Phenyl-beta-naphthylamine				25	25			
P Phenylenediamine					.5			
Hexyldecanol						3		
Al Flake								
Lime	1	1	1	1.5	1.5	1	1	1
Litharge	3							
Sulphur	3	3	3	3	3	3	3	4
White Lead								
Zinc							3	
Diphenylguanidine							2	2
Barytes								18
Total	100	100	100	100	100	100	100	100
Sp. Grav. Cost and Prices								
Cure	30/40	30/40	35/40	29/40	20/40	27/30	Too much Accelerator		15/30
Stretch	8 3/4	8 1/4	9 1/2	12 1/4	9 1/2	8 1/2			10 1/4
Strength	430	405	530	415	450	670			720
Set	3/4	5/16	9/8	1/2	5/16	3/16			5/8
Color									
Date	July 26-18	July 26-18	July 26-18	July 26-18	July 26-18	July 26-18			2-21-19
Remarks							Over cured Too much Accelerator		Compared with 2005 A

NUMBER X 2006 MADE FOR P. O.

		A	B	C	D	E	F	G	H
S. Sheets	50	50	60						
Coarse									
Caucho									
Guayule									
A									
B									
C									
D									
F									
G									
Al Flake									
Lime									
Litharge	10	8	8						
Sulphur	3	3	3						
White Lead									
Zinc	37	37	37						
HERA.		2							
EXCELSIOR Kauba New York City			2						
Total	100	100	100						
Sp. Grav. Cost and Prices									
Cure									
Stretch									
Strength									
Set									
Color									
Date									
Remarks									

NUMBER X MADE FOR P O

		A	B	C	D	E	F	G	H
S. Sheets	42/40	44/40	40/40						
Coarse	14 3/4	15"	15"						
Caucho	2740	2770	2145						
Guayule	3/8	3/4	3/8						
	34/40	34/40	38/40						
	15 3/4	14	15 1/2						
	2480	2255	3090						
A	7/8	9/32	1/4						
B	34/40	34/40	40/40						
C	15 1/2	15"	15 3/4						
D	2000	2000	2250						
F	5/16	1/4	5/16						
G	49/50	49/50	49/50						
	15 1/2	15 1/2	15 1/2						
	2390	2400	2600						
	5/16	9/32	1/4						
	30/30	30/30	30/30						
Al Flake	17	15 1/2	16						
Lime	2000	1920	2300						
Litharge	3/8	9/32	1/4						
Sulphur									
White Lead									
Zinc									
Total									
Sp. Grav. Cost and Prices									
Cure									
Stretch									
Strength									
Set									
Color									
Date									
Remarks									

COMPARISON OF

NUMBER X 1007 MADE FOR ACTION OF ACCELERATORS P. O. _____

		A	B	C	D	E	F	G	H
S. Sheets	10	10	10	50	50	50			
Coarse									
Quicks									
Oxzyole									
HEXA (NEW)	1			1					
P-PHENYLENE		1			1				
A									
B									
C									
D									
F									
G									
S	57	57	57						
Al Flake									
Lime									
Litharge	10	10	11	10	10	10			
Sulphur	2	2	2	3	3	3			
White Lead									
Zinc	20	20	20	37	37	37			
Total	100	100	100	101	101	100			
Sp. Grav. Cost and Prices									
Cure									
Stretch									
Strength									
Set									
Color	Bl.	Bl.	Bl.						
Date	3/24-17	3/24-17	3/24-17	3/26-17	3/26-17	3/26-17			
Remarks									

NUMBER X _____ MADE FOR _____ P. O. _____

		A	B	C	D	E	F	G	H
S. Sheets	30/40	30/40	30/40	30/40	30/40	30/40			
Coarse	6 3/4	6 1/2	7 3/4	15	18 3/4	15 1/2			
Quicks	985	635	692	2195	2450	1950			
Oxzyole	3/16	1/4	3/16	5/16	1/4	1/4			
	25/40	25/40	25/40	45/40	45/40	45/40			
	6 3/4	6 1/2	7	15	18 3/4	15			
	968	668	718	2610	2170	2795			
A	5/16	3/16	3/8	3/8	5/16	3/8			
B	35/40	35/40	35/40	55/40	55/40	55/40			
C	7 1/4	7	5	17 1/2	17	15			
D	616	612	660	3090	3690	2835			
F	7/16	3/8	1/2	1/2	3/4	3/8			
G	35/40	35/40	35/40	65/40	69/40	65/40			
	6	5 3/4	6 1/2	15 1/4	18 1/2	15 1/4			
	910	625	617	3056	3950	3025			
	5/16	3/16	5/16	3/8	3/4	1/2			
	49/40	49/40	49/40	79/40	79/40	79/40			
Al Flake	6 3/4	6 1/4	7 1/2	15 1/4	14	14 1/2			
Lime	746	670	693	2550	2650	2535			
Litharge	3/8	1/4	3/8	1/2	1/4	7/16			
Sulphur									
White Lead									
Zinc									
Total									
Sp. Grav. Cost and Prices									
Cure									
Stretch									
Strength									
Set									
Color									
Date									
Remarks									

NUMBER X 2008 MADE FOR P. O.

		A	B	C	D	E	F	G	H
S. Sheets									
Coarse									
Caucho									
Guayule									
A									
B									
C									
D Sht.	~~93~~	93		93					
F									
G									
USAM	93		93						
Al Flake									
Lime	1	1	1	1					
Litharge			2	2					
Sulphur	4	4	4	4					
White Lead									
Zinc									
HEXA	2	2							
Total	100	100	100	100					
Sp. Grav. Cost and Prices									
Cure									
Stretch									
Strength									
Set									
Color									
Date									
Remarks									

NUMBER X MADE FOR P. O.

		A	B	C	D	E	F	G	H
S. Sheets	30/40	34/40	34/40	34/40					
Coarse	9	7 5/8	8 3/4	7 1/2					
Caucho	950	650	970	570					
Guayule	3/16	1/16	3/16	1/16					
	34/40	34/40	30/40	34/40					
	10 1/2	7 1/2	12 1/4	9 3/4					
	1180	570	1250	640					
A	11/32	1/16	3/8	1/8					
B									
C									
D									
F									
G									
Al Flake									
Lime									
Litharge									
Sulphur									
White Lead									
Zinc									
Total									
Sp. Grav. Cost and Prices									
Cure									
Stretch									
Strength									
Set									
Color									
Date									
Remarks									

NUMBER X 2009 MADE FOR C_6H_5 P. O.

		A	B	C	D	E	F	G	H
S. Sheets	60	60							
Coarse									
Cassia									
Guayule									
Rx Crepe			20	20					
A									
B									
C									
D Sfm			40	40					
F									
G									
Al Flake									
Lime	2	2							
Litharge			10	12					
Sulphur	4	4	3	3					
White Lead									
Zinc	12	12	17	17					
BARYTES	20	22	10	10					
C_6H_5	2		2						
Total	100	100	100	100					
Sp. Grav. Cost and Prices									
Cure									
Stretch									
Strength									
Set									
Color									
Date	4/20-17	4/20-17	4/21-17	4/21-17					

Remarks

NUMBER X MADE FOR P. O.

		A	B	C	D	E	F	G	H
S. Sheets	64/40	64/40	3 9/40	3 9/40					
Coarse	17	17	11 3/4	11					
Cassia	1500	1605	1333	1352					
Guayule	4/4	7/8	1/4	7/16					
	5 3/40	5 3/40							
	16 1/2	16							
	2000	1410							
A	5/16	3/8							
B	7 9/40	7 9/40							
C	17 1/2	17							
D	2810	2090							
F	9/32	3/4							
G	6 9/40	6 9/40							
LOOKS	16	17							
GOOD	2750	1305							
	7/8	3/8							
Al Flake									
Lime									
Litharge									
Sulphur									
White Lead									
Zinc									
Total									
Sp. Grav. Cost and Prices									
Cure									
Stretch									
Strength									
Set									
Color									
Date									

Remarks

NUMBER X 2010 MADE FOR Excelsior From K&B P. O.

		A	B	C	D	E	F	G	H
S. Sheets	50	60	40	40					
Coarse									
Canabo									
Gunyule									
Br Crepe									15
Batanga									40
U Sam									11
A									
B									
C									
D									
F									
G									
MRX.			5	10					
Al Flake									
Lime									2
Litharge									
Sulphur	3	3	3	3					3
White Lead									
Zinc	45	47	47	47					27½
Excelsior	2		2						
Trifon									1
Quartz									½
Total	100	100	100	100					
Sp. Grav. Cost and Prices									
Cure									40/40
Stretch									14
Strength									1605
Set									7/16
Color									
Date	5-7-17	5-7-17							Sept 6-19
Remarks									

NUMBER X 2010 MADE FOR Accelerator and Kodak P. O.

		A	B	C	D	E	F	G	H
S. Sheets									
Coarse									
Canabo									
Gunyule									
Batanga					12	12	40	40	40
U Sam					70	70	11	11	11
A									
B									
C									
D Shelby	93	93	70	70					
F									
G									
Br. Crepe			5	5			15	15	
									15
Thongthrowed Al Flake		1	1						
Lime	1			1	1		2		2
Litharge	3	3							
Sulphur	3	3	4	4	3	3	3	3	3
White Lead									
Zinc							26½	28½	27½
Bayfield			20	20					
Delhi					13	13			
Trifon					1	2	2	2	
Quartz							½	½	½
Diffendorf									
Total	100	100	100	100	100	100	100	100	100
Sp. Grav. Cost and Prices									
Cure	30/40	30/30	30/30	35/35	35/35	35/35	40/40	40/40	30/35
Stretch	7¾	9	8¼	8½	14	14	13¾	13¾	14-16
Strength	510	575	585	675	1525	1620	2105	2075	2530
Set	1/4	7/16	7/8	9/16	13/16	13/16	1/2	7/16	1/2
Color									
Date	3-4-19	3-4-19	3-5-19	3-5-19	3-5-19	3-5-19	3-21-19	3-29-19	3-29-19
Remarks									

NUMBER X 2011 MADE FOR X-1708 A X-1708 B X-1708 C P O

		A	B	C	D	E	F	G	H
B. Sheets	50	50	39.625						
Coarse Para				23.25	32.	35.75	27.5	27.5	27.5
Caoba			5.	10.	10.	10.	10.	10.	10.
Guayule									
Brown Crepe			36.	36.	36	36.	36.	36.	36.
Matalena			16.625	12.	17.	13.	12.	12.	12.
Juertia							10.		
V-55 A		1							
B									
C									
D									
F									
G								10.	
Lithophone									10.
Barytes									
Al Flake									
Lime									
Litharge									
Sulphur	4	4	4.25	4.25	.5	5.25	4.5	4.5	4.5
White Lead									
Zinc	44	43	14.5	14.5					
MgO	2	2							
Rubber	50 %	50%	81%	81.07%	94.745%	94.555%	85.32%	85.32%	85.32%
Sul to Rub.	8 %	8%	5.25%	5.24%	5.28%	5.55%	5.28%	5.28%	5.28%
Accel to Rub.		2%	0.368%	0.222%	0.27%	0.206%	0.211%	0.211%	0.211%
Coef of Fric	240%		2.117	2.47	3736	3441		4.00%	3.02%
Total	100	100	100	100	100.	100	100	100	100
Sp. Grav. Cost and Prices	1.55		1.09	1.09	Floating	Floating			
Cure	80@40'		50@47'	50@47'	65@47'	65@47'	65@47.2h	65@47'	65@47'
Stretch	16		630 %	1974 %	20		Undercured	20	20
Strength	3205		2605	3260, 3290			Stiff-weak	3138	2448
Set	18/32						No good	3/16	3/16
Color	White		grey	grey	Black		Low tensile	grey	Black
Date	6-13-17		6-16-17	6-14-17	6-14-17		6-14-17	6-24-17	6-24-17
Remarks	X	X	X	X	X	X	X	X	X

NUMBER X 2012 MADE FOR P O

		A	B	C	D	E	F	G	H
B. Sheets		9.5					50		
Coarse Para	29.25	16.	31	27.69	23.05	22.34		28	26.27
Caoba	10.	17.	10	10.	10.	10.		10	10.
Guayule									
Brown Crepe	36.	10.	35	35.	16.	13.		35	36.
Matalena	15.		19	22.06	19.33	18.30		22	18.
W. R. X.	5.					5			5.
A									
B									
C									
D									
F									
Paragol					12.	12.			
Guayule		9.							
Ceylon 1st		15.			15.	15.			
Cromite		2.5							
Black Sub		12					1		
V-52 Al Flake									
Lime		1.							
Litharge									
Sulphur	4.75	6.	5	5.25	4.62	4.36	4	5	4.75
White Lead									
Zinc							43		
Magnesia		2.					2		
Rubber	90.525%	78.52%	94.715%	94.419%	83.09%	78.365%	50 %	94.67%	90%
Sul to Rub.	5.26%	7.84%	5.28%	5.56%	5.56%	5.56%	8%	5.28%	6.26%
Accel to Rub	0.244%	3.27%	0.30%	0.35%	0.35%	0.35%	2%	0.348%	0.86%
Coef of Fric	3.79	4	4.12	3.24	F.S. 1.24%	F.S. 1.10%			
Total	100	100	100	100	100	100	100	100	100
Sp. Grav. Cost and Prices	1.21	1.21		1.21	1.21	1.21	1.53	0.958	1.21
Cure	45@47' 55@47'	60@55@47.2h	55@47'	65@47'	55@47'	55@47'	90@4h	55@47'	55@47'
Stretch	20	Both weak undercured	Undercured	18 %	Undercured	Undercured	14	20	21
Strength	2155		2170	2575	Stiff-weak	Stiff-weak	3239	2500	1976
Set	3/16		1/32	1/16	No elong.	No elong.	5/32	1/8	1/4
Color	Black		Black						Black
Date	6-26-17		6-26-17	6-26-17	7-6-17	7-6-17	7-6-17	7-9-17	7-10-17
Remarks	X	X	X	X	X	X	X	X	X 20

NUMBER X 2013 MADE FOR P. O.

		A	B	C	D	E	F	G	H
S. Shorts								50	
Coarse Red	38.27	14.65	21.82	21.	27.75	25.	13.30		23.5
Cascho	10.	10.	10.	10.	10.	10	10.		10.
Graycle									
Brown Cuppa	36	13.	13.	13.	35.	35	13.		30.
Natalena	21.	26.	18.13	17.87	22.	22.	25.45		21.
W.H.R.	5.	5	5.	5.			5.		5.
Parasol		12.	12.	12.			12.		
Coupons		15.	15.	15.			15.		
C									
D									
F									
G									
Ulexa		Fine Sulphur = 1.27%	Fine Sulphur = 1.27%	(No good)	Fine Sulphur = 1.63%	Same as X-2012-G	Med. Fine Sulphur = 0.24%	Med. Fine Sulphur = 2.46%	Fine Sulphur = 0.33%
Al Flake								1	
Lime									
Litharge									
Sulphur	4.73	4.35	5.05	6.13	5.25	5	4.25	4.	4.5
White Lead									
Zinc								43.	
Magnesia							2.	2	
Rubber	89.95%	78.24%	77.68%	76.60	94.42%		76.37%	90%	90.85%
Sul. to Rub	5.26%	5.56%	6.50%	8.00%	5.36%		5.56%	8%	5%
Accel. to Rub	0.30%	0.30%	0.35%	0.35%	0.35%		0.30%	2%	0.35%
Conf. of Vuls	3.84%	13.27%			3.84%		4.73%	3.08%	4.62
Total	100	100	100	100	100.	100	100	100	100
Sp. Grav. Cost and Prices	1.1				0.96		1.1	1.55	
Cure	55@47#	55@47#	55@47#	55@47#	55@47#	55@47#	55@47#	55@47#	55@47#
Stretch	Same as Cond. Set X-2012-F	Was Cured, Was Uneven	Cured Was Uneven	Over Cured Rotten	18¾	Same as X-2012-F	17	14½	19½
Strength		Adjustment	Adjustment	x 9	2575		1923	3372	1890
Set		Was Uneven	Was Uneven		5/16		1/8	3/32	3/32
Color							Black		Black
Date	7-9-17	7-10-17	7-11-17	7-12-17	7-17-17	7-17-17	7-18-17	7-18-17	7-18-17
Remarks	X	X	X	X	X	X	X	Y	Y

NUMBER X 2014 MADE FOR P. O.

		A	B	C	D	E	F	G	H
S. Shorts		35	32	50.		50	50		
Coarse	23.27	23.99		17.	23.25				
Cascho	10.	10.			10.				
Graycle									
B. Cuppa	36.	36.	45		40.				
Natalena	21.	17.43	.18		17.				
W.H.R.		8.			5.				
Parasol	5.								
Powder				15.					
Coupons									
Long Blend				35					
F									
G									
V-62				50					
V-62								1	
V-61						1			
Al Flake									
Lime									
Litharge									
Sulphur	4.73	4.58	5	2.75	4.75	4	4		
White Lead									
Zinc				145		43	43		
Magnesia						2	2		
Rubber	89.95%	87.15%	94.73%	67%	89.99%	50%	50%		
Sul. to Rub	5.26	5.26%	5.27%	4.28%	5.28%	8%	8%		
Accel. to Rub	0.3	0.30%	0.30%	0.47	0.28%	2%	2%		
Conf. of Vuls	4.67%			2.46	4.39%				
Total	100	100	100	64.10	100	100	100		
Sp. Grav. Cost and Prices	1.1	1.1			0.96	1.55			
Cure	53@47#	55@47#	53@47#	55@47#	55@47#	55@40#	40@40#		
Stretch	19¼	19¾	19¼	15½ in.	18 in.	15½			
Strength	2063	1990#	2290	2650	1905#	2189			
Set	1/8	3/32		5/16 in.	3 in.	3/32			
Color	Black			Grey	Black	Brt.			
Date	7-19-17	7-21-17	7-26-17	7-31-17	7-31-17	8-17-17	8-17-17		
Remarks	X	X	X	X	X	X	X		

Uniform

Same as X-2012-F

Vulcanizing

NUMBER X 2015 MADE FOR Stock Intaining 93 S. P. O

		A	B	C	D	E	F	G	H
S. Sheets	78.								
Cosyos									
Cascbo									
Guayule									
Natalina	18.								
A									
B									
C									
D									
F									
G									
Al Flake									
Lime									
Litharge									
Sulphur	4.								
White Lead									
Zinc									
Total	100								
Sp. Grav. Cost and Prices									
Cure									
Stretch									
Strength									
Set									
Color									
Date	9-17-17								
Remarks									

NUMBER X 2016 MADE FOR P O

			A	B	C	D	E	F	G	H
S. Sheets										
Cosyos										
Cascbo										
Guayule										
Pale Ceylon	73.	94.67								
Natalina	22									
V-5-5		.33								
A										
B										
C										
D										
F										
G										
Al Flake										
Lime										
Litharge										
Sulphur	5.	5.								
White Lead										
Zinc										
Total	100	100								
Sp. Grav. Cost and Prices										
Cure										
Stretch										
Strength										
Set										
Color										
Date	9-21-17	9-21-17								
Remarks										

NUMBER X 2017 MADE FOR Aerators P. O.

#		A	B	C	D	E	F	G	H
S. Sheets	50.	50.	50.	50	50.	50.			
Coarse									
Cumbe									
Graysite									
Thionera						1.			
Dyomich					1.				
A									
B									
C									
D									
F									
V-80				1					
V-83			1.						
V-118		1.							
V-57	1.								
Magnesia	2.	2.	2.	2.	2.	2.			
Al Flake									
Lime									
Lithage									
Sulphur	4.	4.	4.	4.	4.	4.			
White Lead									
Zinc	43.	43.	43.	43	43	43.			
Total	100	100	100	100	100.	100.			
Sp. Grav. Cost and Prices									
Cure	50'@40#	40'@40#	60'@40#						
Stretch	14½	14in.							
Strength	3150#	3070#							
Set	7/8	1/4							
Color									
Date	9-28-17	10-2-17	10-5-17	10-4-17	9-30-17	10-2-17			
Remarks	†	†	†						

NUMBER X 2018 MADE FOR Inner Tubes P. O.

Grey + Transparent

#		A	B	C	D	E	F	G	H
S. Sheets		75.25	62.	75.	69.75	69.75	93.5	69.75	99
Coarse									
Cumbe									
Graysite									
Cale Cryla	84.75								
Ulexa	1.								
Inertia	.25	.25			.25	.25		.25	
Natalene		15.	13.	38.					
Whiting				20.	20.	20.		20.	18.
C									
D									
F									
G									
Paraloid		5.			5	3.		4.	
Magnesia	1.00								
Al Flake									
Lime							.5		
Lithage									
Sulphur	5.	4.5	5.	5.	5.	5.	6.	5.	5.
White Lead									
Zinc	8.					2.		1.	
Rubber	84.76%						93.5		
Lead to Rub.	5.90%						55		
Cacal to Rub.	1.18%						✓		
Free Sul	2.44%						1.23%		
Comb. Sul	2.52%						3.49%		
Total	100.	100	100	100	100	100.	100.	100.	100
carg of Vulc.	3.20%								
Sp. Grav. Cost and Prices									
Cure	90@284#	90@284#	100@284	90@286	80@284	85@284	70@284	55@284	
Stretch	19in.	19	18½	18½	16	20	18	20in.	
Strength	2775#	1800	2125	2760#	2705	2775	2710	2700	
Set	3/32	1/16	1/4	1/8	3/32	1/4	1/8	3/32	
Color	Grey								
Date	10-3-17	10-4-17	10-5-17	10-9-17	10-9-17	10-9-17	10-27-17	10-27-17	
Remarks	3606-3.3.	99/284 - 19½ - 2470 - 3/16 - 3.26.							
	†	†	†	†	†	†			

NUMBER X 2019 MADE FOR Inner Tubes P.O. _____

	A	B	C	D	E	F	G	H
R. Havels	69.75	69.75	78.	85.	93.5	77	78	55
Cuero								
Caucho								
Guayule								
Utahica	20	20.	18.	10.		8	18	10
Thermoplastic Blend	25	25						
A								
B								
C								
D								
F								
G								
Peroxide		5.						
Tyrolith	4.							
Al Flake								
Lime				.5				
Litharge								
Sulphur	5.	5.	4.	5	6.	6	4	5
White Lead								
Zinc	1.							
Rubber						94.19%	95.19%	94.5%
Soft Whites						5.0	6.2	5.2
Acetone Soluble						.28	.28	.15
Free Sulphur						2.32%	1.14%	2.17%
Combined Sulphur						2.68%	2.89	2.53
Total	100	100	100	100	100	2/80	100	100
Sp. Grav. Cost and Prices								
Cure	Undercured	60@286	85@286	85@286	85@284	65@284	85@284	80@284
Stretch	120@279	19 in.	20½	20	20¼	20	21	20¼
Strength	Too long a cure to get	2640	2015	2415	2385	2015	2090	2420
Set		9/32	3/32	5/32	3/32	1/4	1/4	1/4
Color								
Date	10-5-17	10-4-17	10-12-17	10-12-17	10-21-17	7-27-18	7-27-18	7-27-18
Remarks	1	4	4	4	4	4	4	4

#3773-S.S.; 85@284 - 19 in - 2845 # - 9/32 in.

NUMBER X 2020 MADE FOR Red Inner Tubes P.O. _____

	A	B	C	D Too	E	F Fig.	G	H
R. Havels	69.5	75.75	68.	68.	82.	70	82.	82.	82.
Cuero							Sol = 3.6% Total = 4.39%	Sol = 4.53% Total = 4.81%	Sol = 4.72% Total = 4.97%
Caucho									
Guayule									
Utahica									
Utahica	13.		10.	10.		12.			
Amine		10.	5.	5.					
Golden Hub Regular Frazier & Co							18.	10.	
Germany Hub Co.								7.25	16.
F									
G									
Crimson F Hub				18.	18.				
Magnesia		1.							
Peroxide	5.								
Golden Hub	10.		15.	13.					
Al Flake									
Lime									
Litharge									
Sulphur	2.5	5.	2.	2.				.75	2.
White Lead									
Zinc		7.75		2.					
T.R. Red		.5							
Total	100	100	100	100	100	100	100	100	100
Sp. Grav. Cost and Prices									
Cure	Undercured	80@284		155@286	155@286	150@286	155@286	150@286	
Stretch	120@279	16 in.		Both undercured		18½			18½
Strength	Too long a cure to get	2240		The Hub cement used		1590			2390
Set		3/32		contain enough		¼			¼
Color		Red		free sulphur.					
Date	10-5-17	10-5-17	10-9-17	10-10-17	10-11-17	10-11-17	10-11-17	10-11-17	10-12-17
Remarks	1	4	4	4	4	4	4	4	4

NUMBER X 2021 MADE FOR Red Inner Tubes P. O. _____

		A	B	C	D	36[illegible]	[illegible]	[illegible]	[illegible]
S. Sheets	77.25		63.5	62.5	69.5	69.5	69.5	69.5	82.
Coarse									
Caucho									
Guayule									
Ustho	12.		18.	18.	13.	13.	13.	13.	
Pale Crepe		86.25							
Wisp		.75							
A									
B									
C									
golden Fr. Fraguil regular			9.	9.			10.	16.	18.
crimson Fr. G.W.P. Co			8.	8.	10.	10.			
Magnesium		1.							
1401-Scarlet	1.	1.							
Prodorth	5.25				5	4.	5.		
Al Flake									
Lime									
Litharge									
Sulphur	4.5	4	1.5	1.5	2.5	2.5	2.5	1.5	
White Lead									
Zinc		5.		1.		1.			
Rubber								82.3	82
Sulfur to Rubber								601	7.4
Accel. to Rubber								.24	✓
Free Sulfur								353	276
Comb. Sulfur								142	219
Coef. of Vulc.								495	495
Total	100	100	100	100	100	100	100	100.	100.
								100 @ 236	158 @ 82
Sp. Grav. Cost and Price								19	21
								2570	2770
								1/4	1/4
								7-27-18	7-27-18
Cure	100@294	100@284		155@286	100@286	100@286	100@286	100@284	153@286
Stretch	19 1/2	16 1/2		18	19	19	19	19	18 1/4
Strength	1915	2676		2240	2400	2245	2250	2050	1850
Set	1/16	3/32		3/32	1/8	1/8	1/16	0/32	1/16
Color									
Date	10-11-17	10-12-17	10-12-17	10-19-17	10-18-17	10-19-17	12-4-17	12-4-17	12-7-17
Remarks	4	4	4	4	4	-1	4	-1	4

NUMBER X 2022 MADE FOR _____ P. O. _____

		A	B	C	D	E	F	G	H
S. Sheets								82	
Coarse									
Caucho									
Guayule									
Renta #1 (Free S. 225 gl)								18	
A									
B									
C									
D									
F									
G									
Al Flake									
Lime									
Litharge									
Sulphur									
White Lead									
Zinc									
Trial	Ufje Tests on Gray Red Inner Tubes cont. acal.							100	
Sp. Grav. Cost and Price	X2018 F S.C.G.	X2019 E	X2019 F	X2019 G	X2021 H HAB	X2021 G			
Cure	85@284	55@284	85@284	80@284	153@286	100@286			
Stretch	18½-16½-7	19½-18½-15½	22-17-16	19½-18½-6	20-18-15	18½-17½-14½			
Strength	3400-1750-1550	2390-2100-1350	2235-1750-1675	2590-2190-1575	2290-1750-950	2390-2320-1575			
Set	¼-¼-0	5/16-¼-¼	½-5/16-¼	5/16-½-0	¼-5/16-¼	3/16-5/16-¼			
Color									
Date									
Remarks	One week →	3 weeks →	6 weeks →	One week →	3 weeks →	6 weeks →	One week →	3 weeks →	6 weeks →	One week →	3 weeks →	6 weeks →	One week →	3 weeks →	6 weeks →	aged in oven at 53°C. 25

Comparison Carbon Black Washed + Unwashed
+ Inertia)

NUMBER X 2023 MADE FOR Smoked Sheets P.O.

		A	B x-105 S.G.	C	D	E	F	G	H	I
~~Smoked Sheets~~					50	50	50	50	50	50
Coarse			X							
Caucho										
Guayule										
W. L. L.	93.5		50							
UnW. L. L.		93.5		50.						
Δ Brand Carbon Black (Boston Chemical Co. Carbon Co.)										18
A										
B										
C										
D										
F										
G										
W. R. X.			10.	10.	10	10	10	10	10	10
Inertia			18.	18.	~~18~~				18	
Excello Carbon Black Boston Chemical Carbon Black & Carbon Co. Boston						18				
Al Flake							18			
Lime	.5	.5	1.	1.	1	1	1	1	1	1
Litharge			3.	3.	3	3	3	3	3	3
Sulphur	6.	6.	3.	3.	3	3	3	3	3	3
White Lead										
Zinc			15.	15.	15	15	15	15	15	15
Carbon Black L.N. Butler Co			Why the lime, litharge, and sulphur last.					18		
Total	100.	100	100	100	100	100	100	100	100	
Sp. Grav. Cost and Prices										
Cure	85@284°	85@284°	65@53°	65@53°	65/53°	65/53°	65/53°	65/53°	65/53°	65/53°
Stretch	20 in.	19½ in.	16 in.	16¼ in.	15½	15	14¼	14¼	16	16
Strength	1830#	1315#	2570#	2600#	2195	2100	2000	2110	2110	2000
Set	9/32 in.	7/32 in.	1 1/16 in.	1 1/8 in.	1	1	1	1	3/4	15/16
Color		grey	Black	Black	Black	Black				
Date		1-5-17	1-5-18	1-5-18	9-7-18	9-7-18	2/8/19	2/13/19	2/26/19	2/26/19

Remarks

Washed and Unwashed

NUMBER X 2024 MADE FOR Brown Crepe, P.O.

		A	B	C	D	E	F	G	H
~~Smoked Sheets~~									
Coarse									
Caucho									
Guayule									
~~Smoked Sheets~~									
~~Smoked Sheets~~									
Washed B.C.	93.5		50.		78.				
Unwashed B.C.		93.5		50.		78.			
B									
C									
D									
F									
G									
W. R. X.			10.	10.	7.	7.			
Inertia			18.	18.					
Al Flake									
Lime	.5	.5	1.	1.					
Litharge			3.	3.	3.	3.			
Sulphur	6.	6.	3.	3.	5.	5.			
White Lead									
Zinc			15.	15.	8.	8.			
			Why the lime, litharge and sulphur last.						
Total	100	100.	100.	100.	100.	100			
Sp. Grav. Cost and Prices			75 & 5 B		75 & 47				
Cure	Did not cure	Did not cure							
Stretch									
Strength									
Set									
Color									
Date									

Remarks

NUMBER X 2025 MADE FOR Hard Rubber Stock P O.

		A	B	C	D	E	F	G	H
S. Sheets	22								
Coarse									
Caucho									
Guayule									
Natalene	50								
A									
B									
C									
D									
F									
G									
Al Flake									
Lime									
Litharge									
Sulpher	28.								
White Lead									
Zinc									
Rubber	71.25								
Accel. to Rub	1.05								
Sul to Rub	39.25								
Free Sul									
Coef. of Vuls									
Total	100								
Sp. Grav. Cost and Prices									
Cure									
Stretch									
Strength									
Set									
Color									
Date									
Remarks									

Age test of Stock

NUMBER X 2026 MADE FOR Cont Liquid Rubber P O

		A	B	C	D	E	F	G	H
S. Sheets	50	50							
Coarse									
Caucho									
Guayule									
M R X	10	12							
Diverta	15	15							
A									
B									
C									
D									
F									
G									
Al Flake									
Lime	1	1							
Litharge	3	3							
Sulpher	3	3							
White Lead									
Zinc	15	15							
Palm Oil	2								
Liquid Rubber		2							
Total									
Sp. Grav. Cost and Prices			X2026 and X2026A one week aging	X2026 and X2026A two weeks aging	X2026 and X2026A three weeks aging	X2026 and X2026A 5 weeks aging	X2026 and X2026A 7 week aging	X2026 and X2026A 9 weeks aging	
Cure		65/53	65/53	65/53	65/53	65/53	65/53	65/53	65/53	65/53	
Stretch		14½	15¼	14	15	12½	14	11½	12½	8½	10½	6½	9½	8	8	
Strength		2745	3000	2300	3360	2265	2760	2150	2700	1905	1600	990	1305	1175	1225	
Set		½	½	5/8	9/16	9/16	5/8	9/16	7/16	5/8	5/8	3/16	5/8	7/16	½	
Color		Black	Black													
Date		6-11-18	6-11-18	7-1-18	7-8-18	7-15-18	7-29-18	8-12-18	8-26-18							
Remarks				aged in oven at 55°C												

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Acid Resistant

NUMBER X 2027 MADE FOR Stock. P. O. .....

		A	B	C	D	E	F	G	H
S. Sheets									
Coarse									
Caarbo									
Guayule									
Mocha	20	23							
Wetho	5	7							
Amine	5								
A									
B									
C									
D									
F									
G									
Paraffin	5	2.5							
M.P.X	5	5.							
[illegible]									
Lime									
Litharge									
Sulphur	1.5	2.							
White Lead									
Zinc									
Al Flake	40.	40.							
Baryta	18.5	20.5							
Total	100	100							
Sp. Grav. Cost and Prices	Blend up with a mixture of Gutta Percha, Rubber, Resin & Whiting								
Cure									
Stretch									
Strength									
Set									
Color									
Date	3-27-18	3-28-18							
Remarks									

NUMBER X 2028 MADE FOR Compressed Asbestos Sheet & Packing Co. Elizabeth, N.J. & Chicago, Ill.

		A	B	C	D	E	F	G	H
S. Sheets	50	50	50	50	50	50	50	50	50
Coarse									
Caarbo									
Guayule									
Granite	2	2	2					2	
Fibre & Asbestos Rayon				2 (Butcher)					2 (White)
A									
B									
C									
D									
F									
G									
Prepared Hexamethylene Tetramine (Smart Weiring) " Recrystallized					1	1	1		
Al Flake									
Lime									
Litharge									
Sulphur	3	3	3	3	4	4	4	3	3
White Lead									
Zinc	47	47	47	47	43	43	43	47	47
Magnesia					2	2	2		
Total	102	102	102	102	105	100		102	102
Sp. Grav. Cost and Prices									
Cure	50/40	50/40	50/40	50/40	50/40	50/40	50/40	50/40	50/40
Stretch	13	13	13	13	13	13	13 1/2	10 1/2	10
Strength	1755	1970	2057	2055	1905	1770	2660	3283	3250
Set	5/16	5/16	5/8	5/16	7/16	3/16	5/16	9/16	5/16
Color									
Date	4-13-18	4-13-18	5-7-18	5-7-18	10-6-18		10-16-18		
Remarks									

NUMBER X 2029 MADE FOR Test Recipes for Glue P. O. _____

		A	B	C	D	E	F	G	H
B. Sheets	15	22	42	50	50	30	37		
Coarse									
Casein									
Guayule									
Linseed Oil	35	35							
Wood Rosin			8	8					
Gum [illegible]						20	20		
A									
B									
C									
D									
F									
G									
Ginger								36	43
M Glue								14	14
Al Flake									
Lime									
Litharge	[illegible]	[illegible]	[illegible]	10	10	10	10	10	10
Sulphur	3	3	3	3	3	3	3	3	3
White Lead									
Zinc	37	30	37	29	37	37	30	37	30
Total	[illegible]	[illegible]	[illegible]	[illegible]	100	100	100	100	101
Sp. Grav. Cost and Prices									
Cure	30/50#	30/50#	30/50#	30/50#	30/50#	30/50#	30/50#	30/40	30/40
Stretch	13½	13	9½	11	13½	11½	12½	13½	14½
Strength	2355	2435	1350	1515	2800	2380	2640	1950	2735
Set	½	½	¼	¼	½	9/16	9/16	½	½
Color									
Date	4-27-18	4-27-18	4-27-18	4-27-18	4-27-18	4-30-18	4-30-18	5-2-18	5-2-18
Remarks									

NUMBER X 2030 MADE FOR Action of Organic Compounds in a Pure Gum Stock. P O _____

	Standard Recipe	A	B	C	D	E	F	G	H
B. Sheets	90. (#3793)								
Coarse									
Casein									
Guayule									
A									
B									
C									
D									
F									
G									
Al Flake									
Lime	1.								
Litharge									
Sulphur	9.								
White Lead									
Zinc									
Free Sulphur Carb. of Rosin									
Total	100								
Sp. Grav. Cost and Prices									
Cure	85/285#								
Stretch	19½								
Strength	2708								
Set	9/16								
Color									
Date									
Remarks									

NUMBER X 2031 MADE FOR Cocalabetortests P O. _____

	A	B	C	D	E	F	G	H	I
S. Sheets	50	50	50	50	50	50	50	50	50
Starch									
Casein									
Oxzyole									
Finger Spool A		1							
" " B			1						
" " C				1					
" " D					1				
" " E						1			
" " F									
Fornicl #999							20	37.3	1
Al Flake									
Lime									
Lithorge									
Sulphur	4	4	4	4	4	4	4	4	4
White Lead									
Zinc	44	43	43	43	43	43	43.7	43.5	43
Zinc Ox	2	2	2	2	2	2	2	2	2
Total	100	100	100	100	100	100	100	100	100
Sp. Grav. Cast and Press									
Cure	58/40	58/40	58/40	58/40	58/40	58/40	58/40	20 40	60/40
Stress	12	13 1/2	15	15	15	14 1/2	15	15	15
Strength	1255	1255	1965	2020	1940	2655	2725	2860	2995	2895
Set	1/16	1/16	1/16	1/16	1/16	1/16	1/16	1/16	1/16
Color	Light Straw	Light Straw	Light Straw	Light Straw	Light Straw	Light Straw	Light Straw		
Odor									
Remarks									

NUMBER X 2032 MADE FOR Comparison Stearine Oil Zinc Oxide P O. Gulf Refining Co

	A	B	C	D	E	F	G	H
S. Sheets	50	50	50	45	43	50	50	50
Starch								
Casein								
Oxzyole								
Delete				32				
Dr Soot (Vanderbilt)					32			
A								
B								
C								
D								
E								
F								
G								
Zinc Ox (Vanderbilt CNJ)						37		
Fornicl								37
Al Flake		37	37				37	
Lime								
Lithorge	10	10	10	10	10	10	10	10
Sulphur	3	3	3	3	3	3	3	3
White Lead								
Zinc	47			10	10			
Chromine		31						
Total	100	100	100	100	100	100	100	100
Sp. Grav. Cast and Press								
Cure	30/40	45/40	30/40	30/40	30/40	30/40	30/40	30/40
Stress	14 3/4	12 1/4	12 1/4	12 1/4	14	14	11	16
Strength	3305	1000	1815	1835	2835	2520	2080	2100
Set	5/16	1/4	1/4	1/4	3/4	7/16	3/16	1/4
Color	Straw	Dark Straw			Straw	Straw		
Odor								
Remarks								

NUMBER X 2033 MADE FOR Pipemouth Stock P O Pipeline

		A	B	C	D	E	F	G	H
S. Sheets	50	23	30						
Coarse									
Cassia									
Guarnie									
Glutton D		27	27						
A									
B									
C									
D									
F									
G									
Al Flake									
Lime									
Litharge	10	10	10						
Sulphur	3	3	3						
White Lead		3							
Zinc	37	37	30						
Total	100	100	100						
Sp. Grav. Cost and Prices									
Cure	30/50	30/50	30/50						
Stretch	15/16	12/16	14						
Strength	3675	2735	2740						
Set	1/2	5/8	1/2						
Color	Dark Grey	Darkkey	Dark Grey						
Date	July 26-1	July 26-1	July 26-1						
Remarks									

NUMBER X 2034 MADE FOR Accelerator test P O

		A	B	C	D	E	F	G	H
S. Sheets	50	50	50	50	50	50	50	50	50
Coarse									
Cassia									
Guarnie									
Chemfillmore		+							
Diphenylguanidine		+							
Methylstearamide			1.5	1	2				
A									
B									
C									
D									
F									
G						2			
Diphenylguanidine						1			
Phenyl-beta-naphthylamine						1	.5	5	
Resistoflex Flower (Flow Aid)									1
Engine Black									
Al Flake									
Lime									
Litharge									
Sulphur	4	4	4	4	4	4	4	4	4
White Lead									
Zinc	43	43	42.5	43	43	43	43.5	43.5	43
Engine	2	2	2	2	2	2	2	2	2
Total	100	100	100	100	100	100	100	100	100
Sp. Grav. Cost and Prices									
Cure	40/45		40/40	25/65		20/30			
Stretch	14/16		14/16	15		14/16			
Strength	2720		3056	3055		3000			
Set	1/2		11/16	1/2		1/2			
Color									
Date	10-22-A		10-22-A	10-22-A		10-22-A			
Remarks									

20/30

14 1/2

3000

1/2

2-10-19

Plaintiff's Exhibit No. 10

32

NUMBER X 2035 MADE FOR Test on Combo Crepe #4235 P. O.

		A	B	C	D	E	F	G	H
S. Sheets									
Coarse									
Uvacho									
Guayule									
[illegible]	50								
[illegible]									
[illegible]		30							
A									
B									
C									
D									
F									
G									
[illegible]			30						
Al Flake									
Lime		1	1						
Litharge		5	5						
Sulphur	3	4	4						
White Lead									
Zinc	47	10	10						
Total	150	100	100						
Sp. Grav. Cost and Prices									
Cure	60/40	50/40	50/40						
Stretch	15 1/2	14 1/4	8 1/2						
Strength	2425	1375	1430						
Set	0/16	3/8	3/8						
Color									
Date	2-10-15	2-11-15	2-10-15						
Remarks									

Comparison of Carrara Filler from Amer. Spreader & Co. Cleveland Ohio roller filler

NUMBER X 2236 MADE FOR Against Al Flake P. O.
Fossil Flour against Tripoli

		A	B	C	D	E	F	G	H
S. Sheets	50	50	50	50	50	50	50	50	50
Coarse									
Cacho									
Guayule									
Mexican White (Rubberized Sheet)						40			
Smith							40		
Light Blue Rubberized Sheet								30	
A									
B									
C									
D									
F									
G									
Fossil Flour Tripoli				30	30				
Carrara Filler		20							
Al Flake	30		30 (O.T. Volume)						
Lime	1	1	1	1	1	1	1	1	1
Litharge	5	5	5	5	5	5	5	5	5
Sulphur	4	4	4	4	4	4	4	4	4
White Lead									
Zinc	10	10	10	10	10			10	10
Whiting									30
Total	100	100	100	100	100	100	100		
Sp. Grav. Cost and Prices									
Cure	60/40	45/40	50/40	50/40	50/40	50/40	50/40		
Stretch	12	14 1/4	13 1/2	8 1/2	12 1/4	14 1/2	15 1/2		
Strength	1370	1920	1290	1435	1470	1935	2465		
Set	1/2	1/2	3/8	3/8	7/16	5/8	1/2		
Color	Gray	Gray	Gray						
Date	12-9-15	12-10-15	12-26-15	4-23-16	4-25-16	5-2-16	5-2-16		
Remarks									

NUMBER X 2037 MADE FOR Mnfr. Supply Co. P. O. Also Selects = Blanket Middlings (Low Grade)

		A	B	C	D	E	F	G	H
R. Rhoeo	50	50	45	45					
Coarse									
Cauebo									
Guayule									
Selects			32						
Blanket Middlings				32					
A									
B									
C									
D									
F									
G									
Al Flake	10	10							
Lime									
Litharge	10		10	10					
Sulphur	5	5	3	3					
White Lead									
Zinc	25	25	10	10					
MnO_2		10							
Total	100	100	100	100					
Sp. Grav. Cost and Prices									
Cure	40/40	10/65	39/40	39/40					
Stretch	14 1/2	14 5/8	14 3/4	14 3/4					
Strength	2775	2200	2520	2525					
Set	3/16	3/4	1/2	1/2					
Color	Black	Gray							
Date	12-26-19	1-2-19	2-10-20	2-10-20					
Remarks									

NUMBER X 2035 MADE FOR Goodyear Tire & Rubber Co. Akron Ohio P. O.

		A	B	C	D	E	F	G	H
R. Rhoeo									
Coarse									
Cauebo									
Guayule									
Selects Blanket Middlings Low Grade		90							
A									
B									
C									
D									
F									
G									
Goodyear	90								
Al Flake									
Lime	1	1							
Litharge									
Sulphur	9	9							
White Lead									
Zinc									
Total	100	100							
Sp. Grav. Cost and Prices									
Cure	30/40	34/40	32/40						
Stretch	11 3/4	8 1/4	11 1/2						
Strength	1235	460	525						
Set	7/8	3/8	1/4						
Color	Gray								
Date	1-25-19	2-20-19							
Remarks	Not used	Used							

NUMBER X 2039 MADE FOR. Tecolostro P O.

		A	B	C	D	E	F	G	H
S. Sheets	50	50	50	50	50	50	50	50	50
Course									
Cassabo									
Guayule									
XTGum 25 pct	1								
XTGum 25 pct		1							
A									
B									
C									
D									
XT. Gum dipping from 1st hopl (2nd crop)					1				
XT. Gum dipping from 1st hopl (2nd crop)						1			
XT. Gum from 1st hopl (crop)			1						
XTGum direct from tree (crop)				1					
Carbonate							1		
Al Flake									
Lime									
Litharge									
Sulphur	4	4	4	4	4	4	4	4	4
White Lead									
Zinc	43	43	43	43	43	43	43	43	43
Magnesia	2	2	2	2	2	2	2	2	2
Phosphorus								1	
Phosphorus Sulphur									1
Total	100	100	100	100	100		100		100
Sp. Grav. Cast and Prime									
Cure	50/40	50/40	60/40	55/40	50/40	50/40	55/40		40/40
Stretch	14½	14½	14½	14½	14½	14½	15		15¼
Strength	2840	3165	2950	3230	3105	3065	2785		2955
Set	4/5	5/8	3/4	3/4	3/4	3/4	5/8		3/4
Color									
Date	1-28-19	1-28-19	2-4-19	2-7-19			1-28-19		2-4-19

Remarks

NUMBER X 2040 MADE FOR Tolaima Sap P O Titanio B

		A	B	C	D	E	F	G	H
S. Sheets	50	50	50	50	50	96½	50	50	
Course									
Cassabo									
Guayule									
Ca. Sap.		44	25	12.5		14			
Gum						3½			
A									
B									
C									
D									
F									
G									
Titanio B-X								45	
Basic White Lead						14			
Al Flake									
Lime							1	1	
Litharge			4	6	6	4			
Sulphur	4	4	4	4	4	8	4	4	
White Lead									
Zinc	44		15	26.5	39	24	45		
Magnesia	2	2		1	1	2			
Total	100	100	100	100	100		100	100	
Sp. Grav. Cast and Prime				1.35	1.55				
Cure				60/45	60/40		55/40	65/40	
Stretch				14½	16¼		14	15	
Strength				2752	2600		2050	2115	
Set		Blank	Blank	1/2	3/4		5/8	3/4	
Color									
Date				1-7-19	2-7-19		Aug 15-19	Aug 19-19	

Remarks

NUMBER X 2041 MADE FOR Compressor Appliance with rubber tube P.O.

		A	B	C	D	E	F	G	H
S. Sheets	50	50	50	50					
Cuorse									
Cuocho									
Onyrals									
A									
B									
C									
D									
F									
G									
Phthroscinal (3)			1	.5					
Phthroscin oil		.5	.5						
Chlorinated Sulphur	.5	.5							
Al Flake	2		2	2					
Lime									
Litharge									
Sulphur	4	4	4	4					
White Lead									
Zinc	435	435	43.5	43.5					
Magnesia		2							
Total	100	100	100	100					
Sp. Grav. Cost and Prices									
Cure	39/40	25/40	35/40	40/40					
Stretch	15	14	14½	14					
Strength	3110	2970	3100	3050					
Set	5/8	9/16	7/8	6/16					
Color									
Date	2-15-19	2-15-19	3-6-19	4m25-19					
Remarks									

NUMBER X 2042 MADE FOR Accelerators P.O.

		A	B	C	D	E	F	G	H
S. Sheets			50	50					
Cuorse									
Cuocho									
Onyrals									
Diphenylguanidine		1							
Triphenylguanidine				1					
Diphenyl Thiourea			1						
A									
B									
C									
D									
F									
G Stolly	68	68							
Hydrolene	10	10							
Lampo	3	3							
Fuel Flour	12	12							
Quercitron	1½	1½							
Al Flake									
Lime	2¼	2¼							
Litharge	1								
Sulphur	2½	2¼	4	4					
White Lead									
Zinc			43	43					
Mag			2	2				1	
Total	100	100	100	100					
Sp. Grav. Cost and Prices	1.64	1.60							
Cure	38/274	20/274	50/40	39/40					
Stretch	3½	3½	16	14½					
Strength	630	620	3035	2890					
Set	4/8	4/8	9/10	5/8					
Color									
Date	2-24-19	3-4-19	1-4-19	1-4-19					
Remarks									

NUMBER X 2043 MADE FOR Comparison M.R. Quartz + Carbon Black P.O. ____

		A	B	C	D	E	F	G	H	
N. Stocks	50	50	50	50	50	50	50	50	50	50
Cosmo										
Coumbo										
Sicksyde								1		
Hydrobine	10									
Aquarius	15	18	18	18	18	18	18	18		18
B.N.R			10						10	10
A										
B										
C										
D										
F										
G										
#15 Peroketa		10								
#8 Peroketa				10						
#23 Peroketa					10					
#20a Peroketa						10				
Al Flake										
Lime	1	1	1	1	1	1	1	1	1	1
Litharge	3	3	3	3	3	3	3	3	3	3
Sulphur	3	3	3	3	3	3	3	3	3	3
White Lead										
Zinc	15	15	15	15	15	15	15	15	15	15
Vulkanox 4010 NA/LG							10			
Vulkanox 4010 NA/LG								10		
Perkacit TBzTD/C									10	
Total	150	100	126	100	100			100	100	100
Sp. Grav. Cast and Press										
Cure	60/53	60/53	60/53	60/53	60/53	60/53		60/53	60/53	60/53
Growth	16	16 1/2	16 1/4	17	17	16 1/2		15	15	15
Strength	2090	2490	2630	2210	2590	2360		2640	2180	2140
Set	1	1	9/8	9/8	13/16	1		1	9/8	1
Color										
Date	3-10-19	3-10-19	3-10-19	3-10-19	3-10-19	3/24/19		5-2-19	5-2-19	5-2-19
Remarks										

NUMBER X 2044 MADE FOR Comparison Pale with white made by other companies P.O. ____

		A	B	C	D	E	F	G	H
B. Blanc									
Cosmo									
Coumbo									
Sicksyde									
Blanc fixe	154/lbs	154/lbs	154/lbs	154/lbs	209				
Cosmic Coupling	4 1/2								
" Nat Rubber &		4 1/2							
" Polybutadiene Engineering			4 1/2						
" Synthetic				4 1/2					
C									
D									
F									
G									
Stearic + 1/2 wax blend					9				
Al Flake									
Lime									
Litharge									
Sulphur	9	9	9	9	18				
White Lead									
Zinc	150	150	150	150	240				
Total	[illegible]								
Sp. Grav. Cast and Press									
Cure	60/40	60/40	60/40	44/40	60/40				
Growth	13 1/2	14 1/2	14 1/2	16	15 1/2				
Strength	860	1950	2235	2/35	2360				
Set	1/4	1/2	6/8	1/2	1/2				
Color									
Date	3-20-19	3-20-19	3-20-19	3-20-19	3-20-19				
Remarks	Blended	Blended	Blended	Blended	Blended				

NUMBER X 2045 MADE FOR Dope & Accelerator P. O.

		A	B	C	D	E	F	G	H
S. Sheets									
Coorse									
Czechs									
Gunyule									
Zinsyn	66.15	63	63	89.5	55			90	
Beaufort Resin		3.15							
Dope 20 Inhibited			3.15						
A									
B									
C									
D									
F									
G									
P Colindine				5	.5	.5	.5		
Batanga						8.5	5.5		9.0
Al Flake									
Lime									
Litharge	7.87	7.87	7.87	4	3	4	2	4	4
Sulphur	2.37	2.37	2.37	6	3 1/2	6	3 1/2	6	6
White Lead									
Zinc					39		39		
Inerting	23.6	23.6	23.6						
Total	99.99	99.99	99.99	100	100	100	100	100	100
Sp. Grav. Cost and Prices									
Cure		35/45	40/45	45/45	60/45	45/45	60/45	55/45	140/45
Stretch		14	13 1/4	19 1/2	15	16	14 1/4	18 1/2	12 1/2
Strength		3570	3135	1995	2420	870	1525	1565	405
Set		7/8	3/4	1/4	1 1/2	3/8	7/16	5/16	3/32
Color		Black							
Date		4-25-19	9-11-19	9-29-19	9-29-19	9-23-19	9-22-19	9-29-19	9-29-19
Remarks									

NUMBER X 2046 MADE FOR M R Compression also Talk Dust & Accel P. O.

		A	B	C	D	E	F	G	H
S. Sheets	50	50	50	50	50	50	50	50	
Coorse									
Czechs									
Gunyule									
Rosin MR #1	10								
Rosin MR #1 Hydrogenated		10							
Inerting	18	18						18	18
A									
B									
C									
D									
F									
G									
Rosin MR #2			10						
Rosin MR #1 Hydrogenated				10					
A.A. Retarder					10				
Talk Dust						18			
Al Flake									
Lime	1	1	1	1	1	1	1	1	
Litharge	3	3	3	3	3	3	3	3	
Sulphur	3	3	3	3	3	3	3	3	
White Lead									
Zinc	15	15	15	15	15	15	15	15	
B.M.R.						10			
MR #1 HH Retarder							10		
MR #2 " "								10	
Total	100	100	100	100	100	100	100	100	
Sp. Grav. Cost and Prices									
Cure	65/53	65/53	65/53	65/53	65/53	65/53	65/53	66/53	
Stretch	15	14 1/2	15	14 1/2	14 1/2	14 1/4	15	15 1/2	
Strength	1635	2195	2255	2100	1930	1485	2215	2170	
Set	3/4	3/8	3/4	3/8	3/4	3/8	1	1	
Color									
Date	4-28-19	4-28-19	4-28-19	4-28-19	4-28-19	6-17-19	7-26-19	7-26-19	
Remarks									

NUMBER X 2047 MADE FOR Comparison B Thistle brand of magnesia P. O.

		A	B	C	D	E	F	G	H	X
S. Shorts	50	50	50	50	50	50	50	50	50	50
Cocoa										
Cassia										
Gunyule										
A										
B										
C										
D										
F										
G										
Magnesia (Thistle brand)	2	2		3	3	3	3	3		
Al Flake	2	4	19-19							
Lime										
Litharge										
Sulphur	4	4	4	4	4	4	4	4	4	4
White Lead										
Zinc	44	44	44	43	43	43	43	43	43	43
Magnesia (Thistle brand)									3	
Al (Thistle Brand)										3
Total	100	100	100	100	100	100	100	100	100	100
Sp. Grav. Cost and Price										
Cure				70/45	75/40	70/45	70/45	80/45	70/45	70/45
Stretch				14 3/4	14 3/4	15	15	15	14 1/2	14 1/2
Strength				2430	2120	3215	2845	2450	3370	2830
Set				5/8	1/2	1/2	5/8	5/8	9/16	7/8
Color										
Date				6-13-19	6-17-19	6-17-19	8-19-19	10-1-19	12-5-19	12-5-19
Remarks										

NUMBER X 2048 MADE FOR Color Compounds P. O.

		A	B	C	D	E	F	G	H
S. Shorts									
Cocoa									
Cassia									
Gunyule									
Ceylon	50	50	50						
A									
B									
C									
D									
F									
G									
Bengal Red	30								
Carbonate Red		30							
Carmine 9 HA			2						
Al Flake									
Lime	3 1/4	3 1/4	3 1/4						
Litharge									
Sulphur	1 3/4	1 3/4	1 3/4						
White Lead									
Zinc									
Comalt	15	15	15						
Whiting			28						
Total	100	100	100						
Sp. Grav. Cost and Price		4							
Cure									
Stretch									
Strength									
Set									
Color									
Date									
Remarks									

NUMBER X 2049 MADE FOR Red Cameron Tubes P. O. _____

		A	B	C	D	E	F	G	H
S. Sheets	85	87 5		92	82				
Coarse									
Caseho									
Guayule									
Kenta #1	18	18							
Indian		.5							
Kenta #2				18					
Kenta #3					18				
B									
C									
D									
F									
G									
Al Flake									
Lime									
Litharge									
Sulphur									
White Lead									
Zinc									
Total	100	100		100	100				
Sp. Grav. Cost and Prices									
Cure									
Stretch									
Strength									
Set									
Color									
Date									

Remarks

NUMBER X 2050 MADE FOR MR Compounding P O

		A	B	C	D	E	F	G	H
S. sheets	50	50	50	50					
Coarse									
Caseho									
Guayule									
M.R X	10								
Quantum	18	18	18	18					
Kenta M.R	Burlam 10	10							
A									
B									
C									
D									
F									
G									
Hardwood Pitch			10	10					
" " "									
Al Flake									
Lime	1	1	1	1					
Litharge	3	3	3	3					
Sulphur	3	3	3	3					
White Lead									
Zinc	15	15	15	15					
Total	100	100	100	100					
Sp. Grav. Cost and Prices									
Cure	65/53	65/53	65/53						
Stretch	17 3/4	17 3/4	15						
Strength	2050	2305	1275						
Set	1 1/2		1						
Color									
Date	8-28-09	8-28-09	9-5-09						

Remarks

NUMBER X 2051 MADE FOR Accelerators for sulphate

		A	B	C	D	E	F	G	H
S. Rhoto									
Coarse									
Caustic									
Quayule									
A									
B									
Sheddy C	93	95	95.5	93.	[illegible]	5			
D									
F									
G									
Rubber						5			
V-5-5		.5		5	.3				
Al Flake									
Lime	1								
Litharge	2								
Sulphur	4	4.5	4.5	4.	[illegible]	4½			
White Lead									
Zinc				2.5					
Total	102	105	100	100		100			
Sp. Grav. Cost and Prices	Standard Rubber Compound								
Cure	40@30#	40@30#	50@40#	20@60#					
Stretch	9in	8¾in	7in	5¾in					
Strength	690#	755	655#	675#					
Set	⅞in	¾	⅝	½					
Color	Black	Black	Black	Black					
Date	8-9-17	8-20-17	8-31-17	8-22-17					
Remarks									

NUMBER X 2052 MADE FOR Hard Rubber Lead alpront valves

		A	B	C	D	E	F	G	H
S. Rhoto									
Coarse									
Caustic									
Quayule									
Zinger	15	10	20						
Kalgan	10	20							
A									
B									
C									
D									
F									
G									
Rubber									
Union	30	30	30						
Al Flake	8	8	8						
Lime	2	2	2						
Litharge									
Sulphur	5	5	10						
White Lead									
Zinc	0½	5	19						
Red Oxide	5½	3	8						
Prussian Blue	3	3	3						
Total	129½	126	130						
Sp. Grav. Cost and Prices									
Cure									
Stretch									
Strength									
Set									
Color									
Date									
Remarks									

NUMBER X 2053 MADE FOR Ilne-Rubber Company P O

		A	B	C	D	E	F	G	H	
S. Sheets	36	43					~~36~~	~~43~~	36	43
Cumo										
Cumbo										
Guayule										
Kang. SS + 3 lbs Bl. Ox. + 3 lbs Calenja Ilne	14	14	14	14	14	14				
A										
B										
C										
D										
F										
G										
Bl. Crepe #130 #131			36	43	36	43	36 14	43 14	36 14	43 14
Al Flake										
Lime										
Litharge	10	10	10	10	10	10	10	10	10	10
Sulphur	3	3	3	3	3	3	3	3	3	3
White Lead										
Zinc	37	30	37	30	37	30	37	30	37	30
Total	100	100	100	100	100	100	100	100	100	100
Sp. Grav. Cost and Prices										
Cure	30/40	30/40	30/40	30/40	30/40	30/40	30/40	30/40	30/40	30/40
Stretch	14	15	12½	14¼	10	12	13¼	13	13¾	11½
Strength	3000	3240	1495	1420	1055	1095	1080	1375	1440	1400
Set	5/8	3/4	3/8	3/8	4/4	3/8	1/8	4/4	3/8	3/8
Color										
Date	19/3/19	19/3/19	19/3/19	19/3/19	19/3/19	19/3/19	23/3/19	23/3/19	23/3/19	23/3/19
Remarks										

NUMBER X 2054 MADE FOR ~~Ilne Rubber Company~~ Ilne Rubber Comparison P O

		A	B	C	D	E	F	G	H
S. Sheets	50	23	30	36	43	36	43	36	
Cumo									
Cumbo									
Guayule									
Shutan D		27	27						
Ilne S			--	14	14				
Ilne R						14	14		
A									
B									
C									
D									
F									
G									
R-Ilne M 500 Innerdal Bl. Ox.								14 36	14 43
Al Flake									
Lime									
Litharge	10	10	10	10	10	10	10	10	10
Sulphur	3	3	3	3	3	3	3	3	3
White Lead									
Zinc	37	37	30	37	30	37	30	37	30
Total	100	100	100	100	100	100	100	100	100
Sp. Grav. Cost and Prices									
Cure				30/40	30/40	30/40	30/40	60/80	60/80
Stretch				14	15	14	14½	11½	12½
Strength				2918	3075	2640	2790	1350	1400
Set				1/2	1/2	7/8	1/2	1/4	5/16
Color									
Date				3-12-19	3-12-19	3-12-19	3-12-19	4-8-19	4-8-19
Remarks									

NUMBER X 2055 MADE FOR Govt Specification 90% Hevea Rubber. P. O.

		A	B	C	D	E	F	G	H
S. Rhodia	90.	78.25	78.25	80.25	80.	80.	84.		
Cumar									
Cumar									
Oxzyde									
Vatalene		12.	12.	10.	10.	10.	6.		
A									
B									
C									
D									
F									
G									
Magnesia							1.		
Powdered			5.25						
Al Flake									
Lime	1.								
Lithopone	4.5								
Sulphur	4.5	4.5	4.5	4.5	4.	3.5	4.		
White Lead									
Zinc		5.25		5.25	6.	6.5	5.		
Rubber	90%	90.07%	90.07%	90.10	89.85%	89.85%			
Acid to Rub.	5%	4.99%	4.99%	4.99%	4.95%	5.90%			
Acid-720	4.33%	80%	220%						
Accel to Rub.		0.167%	0.167%	0.167%	0.167%	0.167%			
Surf of Tube									
Total	100.0	100.00	100.00	100.00	100.	100.0	100.		
Sp. Grav. Cmd and Prime	1.30								
Cure	45#47"	40#47"	65#47"	40#47"					
Stretch	20½"	16½"	30"	14½"					
Strength	2477#	2650#	2693#	2995#					
Set	5/16	9/32	Nil.	Nil					
Color	Black	Brown	Brown	Brown					
Date	8-29-17	8-29-17	8-29-17	8-29-17	9-4-17	9-4-17	10-16-17		
Remarks	1	4	4	4	4	4			

NUMBER X 2056 MADE FOR Gasoline Impervious stock Adhesion test

		A	B	C	D	E	F	G	H - I
S. Rhodia	30	37	30	37	30	37	6	13	17.5
Cumar									
Cumar									
Oxzyde									
Vatalene #1	20	20							
Vat. #2			20	20					
Vat. #3					20	20			
A									
B									
C									
Blue-D							44	44	50 31.25
F									
G									
Al Flake									
Lime									
Lithopone	10	10	10	10	10	10	10	10	10 10
Sulphur	3	3	3	3	3	3	3	3	3 3
White Lead	37	30	37	30	37	30			
Zinc	37	30	37	30	37	30	37	30	31 37
Total	100	100	100	100	100	100	100	100	
Remarks	Good surface Adhesion to Duck = 31.25 lbs Rubber to Rubber = 50 lbs	Adhesion to duck as above Duck = 31.25 lbs Rubber to Rubber = 50 lbs	Adhesion to duck as above Duck = 31.25 lbs Rubber to Rubber = 50 lbs	Adhesion to duck as above Duck = 31.25 lbs Rubber to Rubber = 50 lbs	Adhesion to duck as above Duck = 31.25 lbs Rubber to Rubber = 50 lbs	Adhesion to duck as above Duck = 31.25 lbs Rubber to Rubber = 50 lbs	Adhesion to duck as above Duck = 31.25 lbs Rubber to Rubber = 50 lbs	Adhesion to duck as above Duck = 31.25 lbs Rubber to Rubber = 50 lbs	Adhesion to duck as above Duck = 31.25 lbs Rubber to Rubber = 50 lbs
Cure	30/50	30/50	30/50	30/50	30/50	30/50	30/50	30/50	
Stretch	12"	13"	11¼	13	12	13½	10½	14½	
Strength	2575	2905	2440	2935	2330	2985	2965	3270	
Set	3/16	9/32	1/2	9/32	3/16	9/32	5/8	9/32	
Color	Black	Black	Black	Black	Black	Black	Black	Black	
Date	4-30-18	4-30-18	6-13-18	6-13-18	6-13-18	6-13-18	6-13-18	6-13-18	
Remarks									

NUMBER X 2057 MADE FOR Govt Specification 45% Hevea Rubber P. O. _____

		A	B	C	D	E	F	G	H
S. Sheets	45.	37.	37.	37.	40.	40.	40.		
Coarse									
Caucho									
Guayule									
Hatsleva		8.	8.	8.	5.	5.	5.		
A									
B									
C									
D									
Whiting						6.5	11.5		
Tonolite						30.			
Magnesia					1.	1.	1.		
Black Lead				1.					
Ulexa			.25	.25	.25	.25	.25		
Barytes	10.	10.	10.	10.	10.		10.		
Al Flake	10.	12.75	12.50	11.50	11.50				
Lime	1.								
Litharge	7.								
Sulphur	3.5	2.25	2.25	2.25	2.25	2.25	2.25		
White Lead									
Zinc	23.5	30.	30.	30.	30.	15.	30.		
Rubber	45%	45%	45%	45%					
Sol'd Rub.	7.77%	5%	5%	5%					
Sol'd Rub-Phs	5.55%								
Accel'd Rub.		0.266	0.266	.266%					
Sol'd Vulc-									
Total	100.0	100.00	100.00	100.00	100	100.	100.		
Sp. Grav. Cost and Prices								X 2057 D aged 9 months	X 2057 E aged 9 months
Cure	45@45#	45@45#	45@45#	40@45#	15@60#	15@60#	15@60#	15@60	15@60
Stretch	14½ in	14¾ in	13 in	13 in	13 in	13½	13¾ in	14	14
Strength	2390#	2702#	2900#	2300#	2965#	2910#	3000#	2580	2420
Set	1/32 in	1/32 in	1/32 in	½ in	½ in	½ in	7/16 in	1/2	1/2
Color	~~Black~~	white	white	grey					
Date	8-25-17	8-25-17	8-29-17	9-4-17	11-15-17	11-16-17	11-16-17		
Remarks	4	4	4	4	4	4	4	aged 9 months air. 4	

NUMBER X 2058 MADE FOR Treatment of Sample Lot with Ale P. O. _____

		A	B	C	D	E	F	G	H
S. Sheets									
Coarse									
Caucho									
Guayule									
Hatsleva		93							
A			93						
B				93					
C					93				
D						93			
Whiting							93		
Tonolite									
Magnesia									
Black Lead									
Ulexa									
Barytes									
Al Flake									
Lime		1	1	1	1	1	1	1	1
Litharge		2	2	2	2	2	2	2	2
Sulphur		4	4	4	4	4	4	4	4
White Lead									
Zinc									
Total		100	100	100	100	100	100	100	100
Sp. Grav. Cost and Prices				1					
Cure		30 30	30 30	30 30	30 30	30 30	30 30	30 30	30 30
Stretch		9	9	8½	7½	9½	11	12	11
Strength		345	190	130	125	130	380	315	525
Set		1/16	1/32	0	1/64	1/4	1/16	1/16	1/16
Color									
Date		2-16-18	2-16-18	2-16-18	2-16-18				
Remarks									

Accelerators — Aeroplane Gasoline

NUMBER X 2059 MADE FOR Hose. P. O. ———

		A	B	C	D	E	F	G	H
S. Sheets	20		20.		50	50	50	50	50
Coarse									
Casabe									
Guayule									
Metho	7.	7.	7.	7					
Camsee	5.	5.	5.	5					
Glutan		32.							
M. & R.		5.							
Sinoplast				32					
BMR				5					
D									
F									
G									
Red Oxide		5.	3.	5					
Whiting	35.	13.	32.						
Magnesia	2.	2	2	2	2	2	2	2	2
Antimony	6.5	6.5	6.5	6½					
Al Flake				13					
Lime					1				
Litharge									
Sulphur				1	4	4	4	4	4
White Lead									
Zinc	10.	10.	10.	10	43	43	43	43	43
Tyrolith	14.5	14.5	14.5	14½					
Diffendo (pure)					1				
(35% Ox)						1			
" (14% Ox)							1		
" (3% Ox)								1	1
Total	100.0	100	100		100	100	100	100	100
Sp. Grav. Cost and Prices	Oxide + Co. Asph. Cut 3½ Oil Emulsion 1.2 1.35 2.9								
Cure	48@74°	48@74°	48@74°		20/30	20/30	25/30	20/30	
Stretch	8¾	9¾	9¼		14¼	16¼	14¾	14	
Strength	1125	1360	1540		3450	3490	2790	2580	
Set	9/32	11/32	9/32		3/4	5/8	7/8	7/16	
Color	Red	Red	Red						
Date	2-25-18	2-26-18	2-26-18	8-1-18	10-16-18	10-3-18	11-9-18	11-9-18	

Remarks — Ship. Est

Effect of Benzol and Accelerators in a Rubber Stock

NUMBER X 2060 MADE FOR ——— P. O. ———

		A	B	C	D	E	F	G	H
S. Sheets	50.	50	50	50	50	50			77.5
Coarse									
Casabe									
Guayule									
Accl #301		75							
Accl #305			75						
Accl #310				1					
A							88		
B							3		
C					1				
Frazer Dark									18
F									
G									
Diffendo (pure)					1				
Diffendo (35% Ox)						1	1	½	.5
Eltanga								43	
Magnesia	2.	2	2	2	2	2			
Al Flake								6	
Lime							2		
Litharge									
Sulphur	4.	4	4	4	4	4	6	7	
White Lead									
Zinc	43.	43	43	43	43	43			
Cmk C=OH	1							1	
Oleum								26¼	
Quartzine								16¼	
Celite									
Total		100	100	100	100	100	100		100
Sp. Grav. Cost and Prices							In negligible amt	Color STK	
Cure		50/40	50/40	30/40	20/30	20/30	49/45	35/35	
Stretch		14	16	14	14/15	14/14	19¼		
Strength		2975	3250	2975	3400	3420	26¼		
Set		7/8	13/16	7/8	3/4	7/8	23¼		
Color					White	White			
Date	9-6-18	11-13-18	11-13-18	11-11-18					

Remarks — Accelerator does not blister and tolerance from 2 min. to 5 min. cure

Cured 2 min. at 307° F. and aged 7 days at 158° F. Stopped cure

NUMBER X 2061 MADE FOR Comparison tests for different fabrics of Tennessee Rubber Co.

		A	B	C	D	E	F	G	H
S. Sheets									
Coarse									
Cambo									
Guayule	50								
A Brand " "		50							
Duck " "			50						
A									
B									
C									
D									
F									
G									
Al Flake	16	16	16						
Lime	2	2	2						
Litharge	8	8	8						
Sulphur	4	4	4						
White Lead									
Zinc	20	20	20						
~~Ultramarine~~	~~2~~								
Total	100	100	100						
Sp. Grav. Cost and Prices									
Cure	40/45"	40/30"	95/100						
Stretch	3½	4½	4						
Strength	1250	925	795						
Set	4/16	3/16	3/16						
Color									
Date	4-19-18	4-19-18	4-19-18						
Remarks									

NUMBER X 2062 MADE FOR Treatment of Sound Fabric and Cloth P O

		A	B	C	D	E	F	G	H
S. Sheets									
Coarse									
Cambo									
Guayule									
Fabric soap	85	85							
Pine Tar Oil	15	~~5~~							
Cotton seed oil		10							
A									
B									
C									
D									
F									
G									
Al Flake									
Lime									
Litharge									
Sulphur									
White Lead									
Zinc									
Total	100	100							
Sp. Grav. Cost and Prices									
Cure	30/45	30/60	95/100	90/100					
Stretch	3½	3½	4	4¼					
Strength	745	660	585	545					
Set	1/32	1/32	2/32	1/8					
Color	Gray	Gray	Gray	Gray					
Date	May 15-18	May 15-18							
Remarks									

Comparison 2nd Grade American Zinc Lead & Smelting Co

NUMBER X 2063 MADE FOR + Std Sanitch P. O.

Comparison Lithopone from Mutual Chem. Co

NUMBER X 2064 MADE FOR Accelerators P O

		A	B	C	D	E	F	G	H
S. Sheets	50	50	50	50	50				
Ozone									
Ozonite									
Oxzyde									
A									
B									
C									
D									
F									
G									
Al Flake									
Lime	1	1	1	1	1				
Lithopone	4	4	4	4	4				
Sulphur									
White Lead									
Zinc			45 (illegible)	45 (illegible)	← 45				
Sanitch	45								
Lithopone Hand Blown		45							
Total	100	100	100	100	100				
Sp. Grav. Cost and Prices									
Ozone	50-50	50/40	75/40	75/40	75/40				
Stretch	17	16 1/4	15 1/4	15	15				
Strength	1655	1500	1800	1650	1680				
Set	11/16	9/16	5/8	5/8	3/8				
Color									
Date	9-29-19	9-29-19	10-6-19	10-6-19	10-6-19				
Remarks									

		A	B	C	D	E	F	G	H
S. Sheets									
Ozone									
Ozonite									
Oxzyde									
Zinzyn	57	1	1.5	88.6	50	50	93	55	
Hubbard Russell	1			1.5					
Titanox		89	88.5						55
A									
B									
C									
D									
F									
G									
Diffendo					1		1		
Al Flake									
Lime									
Lithopone	4	4	4	4		1		2	2
Sulphur	6	6	6	6	4	4	6	4	4
White Lead									
Zinc					43	43		39	39
Ozg.					2	2			
Total	100	100	100	100	100	100	100	100	100
Sp. Grav. Cost and Prices									
Ozone	35/45	35/45	26	42	30/6	75/45	70/39	105/45	119/45
Stretch	20	17 1/2	Not enough	Not enough	14	11 1/2	19	14	11 1/2
Strength	2290	1130	Lithopone	Lithopone	2290	1810	2250	1810	985
Set	1/4	1/4			3/8	3/8	1/4	13/32	3/8
Color	Gray	Gray							
Date	10-1-19	10-1-19			10-3-19	10-3-19		11-4-19	11-4-19
Remarks									

NUMBER X 2065 MADE FOR Accelsitors P O

		A	B	C	D	E	F	G	H
S Sheets	5	6	6 1/2	6 0.7	30.5	2 3	5		
Coarse									
Couche	2 1/2	2	2 1/2	2 1.5					
Greyish									
Fourth	5								
Medium	10	10	10	10					
Fifth		2	1		15	15			
Fine Coarse					15				
B									
C									
D									
F									
Coarse						8			
Diffuse				3	5				
Medium Diffuse							7		
Al Flake									
Lime									
Litharge					7	7			
Sulphur	6 1/2	6 1/2	6 1/2	6.25	8	8	4		
White Lead									
Zinc					15	15	4 1/2		
Magnesium	1 1/2	1 1/2		1.25			2		
Calcite					36	24			
Total	25	25	100	100	100	100	100		
Sp. Grav. Cost and Prices									
Cure	65/53	65/53	65/53	65/53	65/53	65/53			
Stretch	15 1/2	15 1/2	10 1/2	9 1/2	11/4	43/4			
Strength	960	1500	1450	2450	2.75	2020	3		
Set	1/8	1/8	1/4	1/8	7/16	3/4	2		
Color									
Date	12-8-13	12-10-13	12-12-13	12-9-13	12-10-13	12-12-13			

Remarks

NUMBER X 2066 MADE FOR Accelsitors P O

		A	B	C	D	E	F	G	H
S Sheets	50	50	50	50	50	50			
Coarse									
Couche									
Greyish									
Diffuse (Coarse)	1								
" (Medium)		1							
" (Fine)			1						
" A (Fine)	1			1					
" B "	2				1				
" C "	3					1			
D									
F									
G									
Al Flake									
Lime									
Litharge									
Sulphur	4	4	4	4	4	4			
White Lead									
Zinc	43	43	43	43	43	43			
Whitening	2	2	2	2	2	2			
Total	100	100	100	100	100	100			
Sp. Grav. Cost and Prices									
Cure									
Stretch									
Strength									
Set									
Color									
Date									

Remarks

NUMBER X 2067 MADE FOR P O

		A	B	C	D	E	F	G	H
S. Sheets		50							50
Coarse									
Carbo	50								
Guayule									
Sunnyside			50	~~50~~		50	50	50	
I A Cuba				50					
A									
B									
Shelby C					95				
D									
F									
G									
Vuelta Corro	1	1	1	1	½				
T P Pl						1			1
Tuxedo							1		
								1	
Al Flake									
Lime									
Litharge									
Sulphur	4	4	4	4	½	4	4	4	4
White Lead									
Zinc	43	43	43	43		43	43	43	43
Mag O	2	2	2	2		2	2	2	2
Total	100	100	100	100	100	100	100	100	100
Sp. Grav. Cost and Prices									
Cure	50/40	50/40	50/40	39/40	5%0	12½	39/40	39/40	3460
Stretch	14¾	14¾	15½	14¼	9	15	14¾	14	15
Strength	1870	2740	2160	1750	630	2600	2000	3560	2300
Rat	¾	¾	½	½	½	½	½	¾	¾
Color	Light Gray	Light Gray	Light Gray	Light Gray	Red Gray	Light Gray	Light Gray	Light Gray	Light Gray
Date	4/28/40	4/22/40	4/27/40	4/20/40	4/24/40	4/26/40	4/25/40	4/27/40	4/27/40
Remarks									

NUMBER X 2068 MADE FOR P O

		A	B	C	D	E	F	G	H 208
S. Sheets									
Coarse									
Carbo	31½	31½	31½	31½		31½	31½	31½	
Sunnyside									52
Sunnyside	60½	60½	60½	60½	90	60½	60½	60½	
Amalgamated and Spanish Combination	½	½							
A Phillipine			½	½					
Wh Plate C P				½		½	½		
" " D. 9							½		
" " F. 1						½			
G								½	½
Tobacco Colonial					1¾				
Al Flake									
Lime									
Litharge									
Sulphur	6¼	6¼	6¼	6¼	6¼	6¼	6¼	6¼	5½
White Lead									
Zinc					1				5
Mag O	1¾	1¾	1¾	1¾	1¾	1¾	1¾	1¾	1
Silete									6
Total	100	100	100						
Sp. Grav. Cost and Prices									35:39 2460 15 ¼
Cure	95/296	75/296	75/296	45/50	25/50	40/50	40/50	45/50	35 30
Stretch	20			18	17	18	19¾	18	17
Strength	2280	1900	1900	3300	3200	2400	2700	2445	3560
Rat	¼			¼	¼	¾	¾	¼	5/8
Color	Lt	Dk	Dk	Light Gray	Black	Light Gray	Light Gray	Light Gray	Light
Date	5/5/40			5/5/40	5/4/40	5/1/40	5/10/40	5/14/40	5/16/40
Remarks									

NUMBER X 2069 MADE FOR Creelsboro P. O.

		A	B	C	D	E	F	G	H
R. Rhode		10				40			5%
Osceo									12
Oneida									
Onayola									
Georgia		30	50	50	40		82	82	15
[illegible]		10			10	10			
Allen		3							
A									
B									
C									
D									
F					½	½	½		½
[illegible]	Regular Trial Stock OKd	1							
[illegible]			5						
[illegible]				2					
[illegible]									
Al Flake		2	10	10	8	8½			
[illegible]						½	½		
[illegible]					5	5			1 Pkg
Sulphur		3	3	3	3	3	3	3	5
[illegible]							7	7	
Zinc		10	10	10	10	10	1	1	2
Pkg 3		1					1	1	2
[illegible]		20	20	20	18	18	5# Wax	[illegible]	
[illegible]		10						5# Wax	
WAX			5	5	5	5			
Naphthalene					½	½			
Total		100	103	100	100		100	100	
Sp. Grav. Cost and Prices	65/55 5 930 ? required [illegible]	30-37 10 1000 ½	1000 ½	890 ¾	[illegible]				
Grav	65/55	30/37	[illegible]	[illegible]	3950	3950	1.0250	1.0250	1.0250
Viscos	15½	13½	11 – 13	13	18	13	17	18	16
Strength	3800	3100	2700-2800	3000	2550	2550	2350	1500	2450
Set	7 5/8	12½	9" – 1	1"	¾	¾	¾	¾	¾
Color	Black	Black	Black	Black	Black	Black	Red	Red	[illegible]
Date	5/23/20	6/23/20	7/26/20	6/26	8/13	8/13	6/22	7/22	[illegible]

Remarks

NUMBER X 2070 MADE FOR Red Tanks P. O.

Wyoming & Blue Rocky Clay

		A	B	C	D	E	F	G	H
R. Rhode	50	50	50						
Osceo									
Oneida									
Onayola									
Georgia				82	92	92	82	82	
[illegible]				½	½				
[illegible]				½					
A									
B									
C									
D									
F									
G									
[illegible]						1			
MAYC							1	1	
[illegible]				½	[illegible] 6	[illegible] 6	[illegible] 6	6	
Al Flake									
Lime	1	1	1						
Litharge									
Sulphur	4	4	4	3	5½	5½	5½	5½	
White Lead									
Zinc		[illegible]		1	5	5	5	5	
[illegible]	[illegible]	45							
Blue Rocky Clay	Clay	[illegible]	45						
[illegible]				7					
Pkg 0				1	1	1	1	1	
Red Shale				5					
Total				100	100	100½	100½		
Sp. Grav. Cost and Prices	1# enough for [illegible]								
Grav	1.0490	80/40	80/40	[illegible]	2.1.1	[illegible]	[illegible]	[illegible]	
Viscos	16	16	10	18 – 18	15	18 – 19	18 19	19	
Strength	1350	1400	1230	2130-2200	4050	2700-3300	1700 2700	3200	
Set	½	½	⅝	¼ ⅝	½	¼ – ⅝	¼ ½	½	
Color				Red	Clay	Clay	Clay	[illegible]	
Date	5/26-27	5-26-20	5-26-20	6/24	6/24/20	6/30/20	6/30/20	[illegible]	

Remarks

Comparison below Znox Sebic

NUMBER X 2071 MADE FOR _____ P. O. _____

		A	B	C	D	E	F	G	H
S. Sheets	43	43							
Cosmo									
Cascho									
Guayule									
A									
B									
C									
D									
F									
G									
Al Flake									
Lime									
Litharge									
Sulphur	3	3							
White Lead	6	6							
Zinc	40	40							
Sebic	8	8							
Total	100	100							
Sp. Grav. Cost and Prices									
Cure									
Stretch									
Strength									
Set									
Color									
Date									
Remarks									

NUMBER X 2072 MADE FOR _____ P O _____

		A	B	C	D	E	F	G	H
S. Sheets	81	81	81	81	81	81	81	81	81
Cosmo									
Cascho									
Guayule			53	81					
A			Blank	5½					
B				6½					
C				6½					
D									
F									
G									
Crowite	½						¼	¼	
Sulphur		½					¼		
Diphenyl			½					¼	¼
Mexa									
Al Flake	Para Red				½				½
Lime	½	½	½		½	½	½	½	½
Litharge									
Sulphur	5½	5½	5½		5½	5½	5½	5½	5½
White Lead									
Zinc	6½	6½	6½		6½	6½	6½	6½	6½
Inertia	6	6	6		6	6	6	6	6
Total	100	100	100	100	100	100	100	100	100
Sp. Grav. Cost and Prices									
Cure									
Stretch									
Strength									
Set									
Color									
Date									
Remarks									

aging of Asbestos Covers

NUMBER X 2073 MADE FOR _____ P O _____

		A	B	C	D	E	F	G	H
S. Shoots	81	81	81	81	81				
Coarse									
Caorbo									
Guayule									
Diaphor	1/2	1/4	1/4	1/8	3/4				
Paraffine		5							
Pd Lin		1/4							
A									
B									
C									
D									
F									
G									
Formaldehyde Asb	1/4								
Dixie Clay			1/4	3/8					
Al Flake									
Lime	1/2	1/2	1/2	1/2	1/2				
Litharge									
Sulphur	5 1/2	5 1/2	5 1/2	5 1/2	5 1/2				
White Lead									
Zinc	1 3/4	6 1/2	6 1/2	6 1/2	6 1/4				
Inerton	6	6	6	6	6				
Mg O	1								
	100	100	100	100	100				
Sp. Grav. Cost and Prices	N G	N G	N G	N G	N G				

Cure
Stretch
Strength
Set
Color
Date

Remarks

NUMBER X 2074 MADE FOR _____ P O _____

	2074 P.J.Z	A	B	C	D	E	F	G	H
S. Shoots	15			15			15		
Coarse									
Caorbo									
Guayule									
Diaphor	19 1/2	10	10	19 1/2	10	10 1/2	19 1/2	20	
Batanga								15	
Wotomin		30	30		40	40			
A									
B									
C		31 1/2	36 1/2		30		40		
D									
F									
Crayllbond	40			40		30		43	
Arama	1			1			1		
Paraffin				1 1/2				2	
B.U.R	5	10	15	3	5	5	4		
Al Flake									
Lime	1			1		1	1	1	
Litharge	8	5	5	5	5	5	8	5	
Sulphur	3 1/2	3 1/2	3 1/2	3 1/2	3 1/2	3 1/2	3 1/2	3	
White Lead									
Zinc	7	10	10	7 1/2	6 1/2	5	7	8	
Ferrite						Tasheet		PS K	
	=P.J.Z								
Total	100	100	100	100	100	100	100	100	
Vol Pounds	(Light)							55	
Sp. Grav. Cost and Prices	1.34	1.43	1.45	1.32	1.43	1.41		1.33	
	13 12	10.04	10.29	13 26	0976	0982		1251	
cu ft	10.96	9.41	950	10.90	8.71	865		10.52	
Cure	35/274	35/274	35/274	35/274	30/274	30/274	30/274	30/274	
Stretch	1350	13	12 1/2	12 1/2	17 1/2	12 1/2	12 1/2	12 1/8	
Strength	1450	1335	165	900	1007	1165	1240	940	
Set	3/4	7/8	7/8	7/8	1	1	7/8	7/8	
Color									
Date	1-2-22				2-22	2-9-22		2-22-22	

Remarks P.J.Z Asphaltic cement 24 # PAR

THE ACTION OF CERTAIN ORGANIC ACCELERATORS IN THE VULCANIZATION OF RUBBER—III[1]

By G. D. Kratz, A. H. Flower and B. J. Shapiro[2]

It has for some time been generally recognized that although aniline is effective as an accelerator in the absence of zinc oxide, diphenylthiourea functions but mildly in the absence of, and strongly in the presence of this substance. Reference to this effect has already been made indirectly in the literature several times, and recently Twiss[3] has given curves for physical test results which demonstrate quite clearly the effectiveness of diphenylthiourea as an accelerator in the presence of zinc oxide. His statement that diphenylthiourea is practically inert in the absence of zinc oxide is, however, not in accord with our findings.

In a previous paper of this series[4] we have shown that in the acceleration of the vulcanization of a rubber-sulphur mixture, the activity of one molecular part of diphenylthiourea is less than that of an equimolecular quantity of aniline, but equal to that of one molecular part of aniline and one molecular part of phenyl mustard oil.

Our former experiments, however, were confined to the determination of sulphur coefficients at one cure only. In the present instance, we desired to compare the relative effects of aniline and diphenylthiourea over a series of cures, and to effect this comparison both by means of the sulphur coefficients and the physical properties of the various mixtures and cures. Further, it was desired to compare mixtures which contained zinc oxide, as well as the rubber-sulphur mixtures previously employed.

Summarizing our results briefly, we found that, in a rubber-sulphur mixture, the accelerating effect of aniline is considerably greater than that of diphenylthiourea, when judged either by sulphur coefficients or on the basis of the physical properties of the vulcanized mixtures. In mixtures which contained zinc oxide, however, the reverse was found to be true, and diphenylthiourea was more active than aniline when judged by either of the above criteria. It was also evident that in the case of the mixtures which contained zinc oxide, although the tensile strength of the mixture which was accelerated by diphenylthiourea increased more rapidly than in the case of the mixture accelerated by aniline, the same maximum tensile strength was attained by each. The sulphur coefficients at their respective maxima were practically identical. While the maximum tensile strength of the rubber-sulphur mixture which was accelerated by aniline was the same as that obtained when zinc oxide was present in the mixture, it was attained only at a much higher sulphur coefficient. Lastly, it was also found that the tensile strengths of the mixtures that contained zinc oxide and which were accelerated by either aniline or diphenylthiourea, particularly the latter, were increased tremendously during the first part of the vulcanization, and at very low sulphur coefficients. This would indicate the possibility of certain substances (accelerators) increasing the physical properties of a vulcanized mixture without greatly affecting the sulphur coefficient.

This point is of interest as it already has been noted by ourselves,[4] Cranor,[6] and others, that with mixtures which contain zinc oxide and a strong organic accelerator, the correct (or optimum) cure is obtained at abnormally low sulphur coefficients when compared with those obtained for unaccelerated mixtures. No explanation has been offered for this phenomenon. Bedford and Scott,[7] however, regard diphenylthiourea as the aniline salt of phenyldithiocarbamic acid after H_2S has been liberated. This salt is extremely unstable, owing to the weakly basic properties of aniline, and in this respect, according to Krulla,[8] is unlike the metallic salts of the same acid. In this connection, it is particularly pertinent to note that Bruni[9] has recently found the zinc salts of the mono and disubstituted dithiocarbamic acids to be violent accelerators. It is quite possible, then, that such a salt may be formed during the vulcanization process in mixtures which contain both diphenylthiourea and zinc oxide,[10] and that, irrespective of its action as an accelerator, the zinc portion of such a salt may be responsible for the physical improvement imparted to the mixture.

Our present results, moreover, particularly when interpreted with the assistance of the excess sulphur coefficients obtained for the various mixtures at different times of cure, show that when aniline is employed as the accelerator in the presence of zinc oxide, the effect of the latter substance is manifested almost entirely in the physical properties of the mixture. When aniline is replaced by diphenylthiourea the reverse is true, and the activity of the original substance as an accelerator is greatly increased when measured by either the sulphur coefficients or physical properties. In the latter instance, then, the zinc oxide most probably either assists in the decomposition of the diphenylthiourea

[1] Presented before the Rubber Division of the American Chemical Society, Chicago, Ill., September 6 to 10, 1920.
[2] The Falls Rubber Co., Cuyahoga Falls, Ohio.
[3] Journal of the Society of Chemical Industry, 39, 1920, 125t.
[4] Journal of Industrial and Engineering Chemistry, 12, 1920, 317.
[5] Journal of Industrial and Engineering Chemistry, 11, 1919, 39; Chemical & Metallurgical Engineering, 20, 1919, 418.
[6] The India Rubber World, 61, 1919, 367.
[7] Journal of Industrial and Engineering Chemistry, 12, 1920, 31.
[8] Ber., 46, 2869.
[9] British Patents Nos. 140,387 and 140,389.
[10] The action of diphenylthiourea with zinc oxide is apparently similar to the action of the natural accelerator with magnesium oxide, as pointed out in a previous paper (Journal of Industrial and Engineering Chemistry, 12, 1920, 971). In both cases the oxide serves in a counterbalancing capacity rather than as a primary accelerator. It is obvious that no one oxide will activate all accelerators equally well.

Plaintiff's Exhibit No. 11 (Page 1)

to a more active substance, or combines with the decomposition or alteration products of the original substance with the formation of a zinc salt, which is responsible for the increase both in the sulphur coefficients and tensile strength of the mixture. Our results with aniline as the accelerator, however, do not indicate the formation of such a salt.

Thus, in the presence of zinc oxide, the activity of aniline and diphenylthiourea as accelerators appears to be of a different nature. Evidently, an acid substance, probably a thiocarbamic acid, capable of reacting with zinc oxide, is formed as one of the decomposition products of diphenylthiourea. The excess accelerating activity is attributed to this zinc salt. When aniline is employed as the accelerator, there is no evidence of such salt formation.

EXPERIMENTAL PART

The present experiments were designed to effect a comparison of the sulphur coefficients and physical properties of representative mixtures when accelerated by 0.01-gram-molecular quantities of either aniline or diphenylthiourea. The six following mixtures were employed for this purpose, and each was vulcanized for a series of cures:

A—Rubber-sulphur control
B—Rubber, sulphur, and aniline
B 1—Rubber, sulphur, and diphenylthiourea
C—Rubber, sulphur, and zinc oxide control
D—Rubber, sulphur, zinc oxide and aniline
D 1—Rubber, sulphur, zinc oxide, and diphenylthiourea

The quantities of each substance employed in these mixtures are shown in Table I. The amounts of aniline or diphenylthiourea added to these respective mixtures represent 0.01 gram-molecule of the accelerator for each 100 gms of rubber in the mixture. Otherwise, the same general method of procedure was adopted in the course of this work as in that previously reported in Part I.[11]

The rubber used was of good quality, first latex, pale crepe, a different sample of the lot used in our former experiments. The various mixtures were mixed on the mill, vulcanized, and tested in the same manner as before. The physical properties of the vulcanized samples were determined on a Scott testing machine of the vertical type, with the jaws opening at the rate of .20 inches per minute. A recovery period of 48 hours was allowed before physical tests were made. Combined sulphur was estimated by our method previously reported in detail.[12]

The various mixtures were vulcanized at 141.5 degrees C. for different intervals of time up to 240 minutes.[13] The sulphur coefficients and physical properties of the different cures for each mixture were determined. These results are given in detail in Table II. Generally speaking, the results obtained were in good agreement, and fairly smooth curves for physical properties were obtained.[14]

Table I

Ingredient	Mixture A	Mixture B	Mixture C	Mixture D	Mixture B 1	Mixture D 1
Rubber	100.00	100.00	100.00	100.00	100.00	100.00
Zinc oxide	....	....	100.00	100.00	....	100.00
Sulphur	8 1	8 1	8 1	8 1	8 1	8 1
Aniline	....	0.93	....	0.93	....	....
Diphenylthiourea	....	....	....	....	2.28	2.28

Table II

(All Mixtures Vulcanized at 141.5° C.)

Cure in Minutes	Mixture A: Sulphur Coefficient	Mixture A: Tensile Strength, Lbs. per sq. in. at Break	Mixture A: Final Length at Break Per Cent	Mixture B: Sulphur Coefficient	Mixture B: Tensile Strength, Lbs. per sq. in. at Break	Mixture B: Final Length at Break Per cent	Mixture C: Sulphur Coefficient	Mixture C: Tensile Strength, Lbs. per sq. in. at Break	Mixture C: Final Length at Break Per Cent	Mixture D: Sulphur Coefficient	Mixture D: Tensile Strength, Lbs. per sq. in. at Break	Mixture D: Final Length at Break Per Cent	Mixture B 1: Sulphur Coefficient	Mixture B 1: Tensile Strength, Lbs. per sq. in. at Break	Mixture B 1: Final Length at Break Per Cent	Mixture D 1: Sulphur Coefficient	Mixture D 1: Tensile Strength, Lbs. per sq. in. at Break	Mixture D 1: Final Length at Break Per Cent
30	0.754	....	....	1.176	545	1180	1.005	....	....	1.431	510	710	0.913	(1)	1210	1.603	2219	820
45	0.936	279	1250	1.317	1019	1170	1.055	306	640	1.490	1356	720	1.063	(1)	1360	1.912	3391	780
60	1.038	....	....	1.563	1228	1120	1.207	392	750	1.628	1819	770	1.335	(1)	1280	2.297	4442	790
75	1.090	494	1220	1.898	....	....	....	....	....	....	1968	750	1.809	533	1230	2.623	....	....
90	1.531	709	1150	2.182	1621	1060	1.338	1041	700	2.382	2350	720	1.953	789	1220	2.962	2730	830
120	2.069	871	1160	2.351	2046	1190	1.765	1815	780	2.801	2908	780	2.496	1053	1210	3.755	2699	778
150	2.256	1159	1130	4.033	2410	1190	2.217	1970	760	3.266	3721	770	3.109	1303	1150	4.521	2619	750
180	2.470	1321	1130	6.939	2670	1030	2.630	2032	750	4.226	3663	740	4.027	1779	1110	5.357	2030	690
210	3.179	1842	1100	5.264	2760	970	3.246	2184	760	4.906	2545	700	4.730	2021	1080	6.379	1118	530
240	3.751	2124	1060	6.268	2131	910	3.615	1978	730	5.364	1837	680	5.624	2362	1050	7.079	754	440

(1) Test pieces did not break.

(2) In mixtures which contain zinc oxide, diphenylthiourea is more active than aniline.

(3) In mixtures accelerated by aniline, either with or without zinc oxide, the same maximum tensile strength is obtained, accompanied by a higher sulphur coefficient in the absence of zinc oxide than when this substance is present.

(4) Mixtures which contain zinc oxide, and which are accelerated by either aniline or diphenylthiourea, show large increases in tensile strength in the early stages of the vulcanization.

(5) Mixtures which contain zinc oxide and which are accelerated by either aniline or diphenylthiourea, attain the same maximum tensile strength at approximately the same sulphur coefficients.

(6) There is apparently no general relation between the physical properties and sulphur coefficients of accelerated mixtures.

[11] Journal of Industrial and Engineering Chemistry, 12, 1920, 317.
[12] The India Rubber World, 61, 1920, 356.
[13] In the experiments described in Parts I and II vulcanization was carried on at a temperature of 140 degrees C.
[14] Satisfactory physical test results for representation graphically are obtainable with considerable difficulty. We have found it necessary, particularly when working on stress-strain diagrams, to employ three men, one to operate the machine and two to take readings.

CONCLUSIONS

(1) In a rubber-sulphur mixture, the activity of aniline in the acceleration of vulcanization is much greater than that of a molecularly equivalent quantity of diphenylthiourea.

SHIPPING SERVICE TO RHINE POINTS RESUMED

The Red Star Line of the International Mercantile Marine Co., New York, N. Y., announces resumption of its pre-war all-water service to points on the River Rhine. Transhipment via fast Antwerp steamers may be made for both incoming and outgoing traffic. Through rates will now be named and through bills of lading issued. Goods for France, Alsace-Lorraine and the district of the Saar may be shipped via Strasburg without assessment of the French Customs surtax. Rates will also be named for rail shipments via Antwerp and Thionville to and from the Rhine Valley, Switzerland, France and inland points in Belgium for handling classes of cargo requiring rail transportation. This restores Antwerp as a shipping point for the territory in question to the same favorable position it held before the war.

Plaintiff's Exhibit No. 11 (Page

T #8

First Lilac	27	0
Sheets	27	- 0
Shd	17	- 13
Brown Lub	7	- 0
M R	7	- 0
Zinc	1	- 12
Blanc Fixe	5	- 6
Sul	5	- 6
# 4 Black	0	- 5
H. Magnesia	0	- 8
Paraffin	0	- 14
	100	

Plff. Exhibit #13
Oct. 15/25
Mills

PLAINTIFF'S EXHIBIT No. 14

IN THE UNITED STATES DISTRICT COURT, SOUTHERN DISTRICT OF NEW YORK

In Equity. No. 24-23

DOVAN CHEMICAL CORPORATION, Plaintiff,

vs.

NATIONAL ANILINE CHEMICAL COMPANY, INC., Defendant

Weiss Patent No. 1,411,231

Affidavit of Clinton A. Carlton

STATE OF OHIO,
County of Richland, ss:

Clinton A. Carlton, being duly sworn, deposes and says as follows:

I am of mature age and reside in Mansfield, County of Richland, State of Ohio. I am employed as Chemist at the Works of the Columbia Tire & Rubber Company, Mansfield, Ohio. I am a graduate of the University of Akron, in the City of Akron, Ohio, at which place I obtained the degree of B. S. in Chemistry in 1917. Immediately after graduating from said University, I was employed by the Republic Rubber Company of Youngstown, Ohio, at which place my work commenced in June of 1917. At the commencement of my work with the Republic Rubber Company, I found it necessary to put the chemical laboratory in better condition for analytical work, and, therefore, immediately ordered various materials and supplies. During my employment at the Republic Rubber Company I was under the direction of Monroe H. Daniels, who was Chief Chemist for said company and was associated with Mr. Morris L. Weiss in connection with my work relating to the preparation and analyses of organic compounds.

At various times during my connection with the Republic Rubber Company of Youngston, Ohio, I had various talks with said Morris L. Weiss concerning accelerators. During one or more of these talks, Mr. Weiss referred to dy-

phenylguanidine which he considered would probably be a good accelerator because it was more basic than triphenylguanidine, with which I had previously been somewhat familiar. In this connection, Mr. Weiss showed me a copy of Richter's Organic Chemistry, to which we had access at the plant of the Republic Rubber Company, and called my attention to a page in said Chemistry which mentioned dyphenylguanidine simply as a known organic compound capable of being produced in a chemical laboratory. This fact serves to fix in my memory the fact that said Morris L. Weiss suggested to me the use of such dyphenylguanidine as an accelerator during my employment with the said Republic Rubber Company. I agreed with Mr. Weiss that it would be worth while testing dyphenylguanidine as an accelator and stated that I thought it would be well for him to proceed with said tests.

I left the employ of the Republic Rubber Company on March 8, 1918, because of the fact that I had been inducted into the Engineers Enlisted Reserve Corps of the United States Army on account of the war conditions which existed at that time, and was temporarily assigned to the University of Akron for the teaching of organic chemistry.

To the best of my knowledge, information and belief, Corl H. Eaton, whom I understand has previously made an affidavit in this cause, was not employed at the Republic Rubber Company during my connection with said company and understand that he entered the employ of said Republic Rubber Company in October 1918, as stated in his affidavit.

At the request of a person whom I understand was a representative of the defendant in this case, I made an affidavit dated June 3, 1922, and the statements made therein are true to the best of my knowledge, information and belief. Said affidavit, however, is not to be interpreted to the effect that Morris L. Weiss did not originally bring to my attention the possible use of dyphenylguanidine as an accelerator.

While employed at the Republic Rubber Company at Youngstown, Ohio, I was acquainted with Carl H. Zieme, but said Zieme was employed in the Hose Department of the Republic Rubber Company and was not in touch with the working of the chemical laboratory or the work undertaken by myself or said Weiss.

According to the best of my knowledge, information and belief, Morris L. Weiss is the first and original inventor of the use of dyphenylguanidine as an accelerator in the vulcanization of rubber and its production in commercial quantities for that purpose.

The above facts were recalled to my mind by a conversation with Mr. Morris L. Weiss at the time of the meeting of the American Chemical Society in Pittsburgh, Pennsylvania, during the first week in September, 1922.

Clinton A. Carlton.

Sworn to and subscribed before me this 7th day of November, 1922. Charles W. Chew, Notary Public, Richland Co., Ohio. Com. expires 12/18/24.

PLAINTIFF'S EXHIBIT No. 17

Report

Name of Co.: Perth Amboy Chemical Works.
Department: Rubber Laboratory.
Subject: Report of proceedings at the Rubber Division Meetings of The American Chemical Society held in Philadelphia—September 3, 4, and 5th.
Author: C. S. Williams.
Date: September 8, 1919.

The writer attended all of the meetings of the Rubber Section and heard practically all of the papers which were read. The majority of these were only of general interest and did not bear directly on our products. The papers of special interest were as follows:

1. J. H. Scott—Action of Accelerators during vulcanization.

This paper dealt primarily with inorganic accelerators.

2. G. D. Kratz, A. H. Flower and Cole Coolidge—Action of certain organic accelerators in the vulcanization of rubber.

This paper was of particular interest in that the writers attempted to explain the action of Hexamethylenetetramine during vulcanization. According to their theory, Hexa-

methylenetetramine is converted during vulcanization into Di-thiourea which is the accelerating agent. They also stated that the action of Formaldehyde Aniline was due to the formation of Thiocarbanilid during vulcanization. The writer wishes to remark that his work with Formaldehyde Aniline and Thiocarbanilid does not confirm the statement of the above authors.

3. C. W. Bedford and Winfield Scott—Reactions of Accelerators during vulcanization.

The authors of this paper stated that the most widely used of all accelerators at the present time was Thiocarbanilid. This paper dealt with the chemical reactions involved during vulcanization.

4. D. F. Cranor—The effect of organic acceleration on the vulcanization coefficient.

This paper was quite academic. An attempt was made to show that the desired vulcanization coefficient was produced in a shorter time with the use of accelerators than without. Mr. Cranor's experiments as reported in this paper compared a control sample with a sample cured with Hexamethylenetetramine and a sample cured with one of the Bayer accelerators. This author informed the writer that it was impossible to use Hexa without the aid of Zinc Oxide. It is impossible to conceive how he arrived at this conclusion since we have found the contrary to be true at our laboratory.

The symposium on the action of accelerators which followed was unimportant as everyone seemed to try to conceal all he knew on the subject but obtained all the information possible from the others.

An interesting industrial trip was made by some of the members of the section, including the writer, to the Lee Tire & Rubber Company, Spring Mill, Pa.

The general outlook for accelerators was quite favorable and it was evident that everyone there realized the necessity of accelerators in all classes of rubber goods. The opinion was expressed that the rubber business during the coming year would be much larger than last year. It was stated that the index for the rubber business is the volume of manufacture in the automobile industry.

The chief value of the meetings which the writer attended lay in the fact that he was able to meet many of the well

known rubber men some of whom are our regular customers and some who we hope to have as customers.

Respectfully submitted.

C. S. W.

CSW/LK.

PLAINTIFF'S EXHIBIT No. 19

American Chemical Journal, 1901—v. 26

Oxygen Ethers of the Ureas

Ethyl phenylisourea, after having been in contact with concentrated aqueous ammonia for two months at the room temperature, was recovered unchanged.

No action could be detected after heating the urea ether in a sealed tube with alcoholic ammonia for three hours at 140°, the urea ether being again entirely recovered.

If ammonia reacted with ethyl phenylisourea according to the above equation, monophenylguanidine would be one of the products. Feuerlein[1] has described a substance as monophenylguanidine, but the properties given are not those one would expect a guanidine to have.[2] For fear from lack of exact knowledge concerning its properties of overlooking the base if it had been formed only in small quantity, it seemed best to prepare the guanidine synthetically. Even after becoming familiar with its properties none could be found when phenylisourea was treated with ammonia.

Monophenylguanidine, $C_6H_5NHC(:NH)NH_2$.—Equivalent amounts of cyanamide and aniline hydrochloride were placed in a sealed tube with double the weight of absolute alcohol and heated at 100° for two and a half hours. The tube opened with no pressure. Its contents were evaporated on the water-bath nearly to dryness and redissolved in a little water. Addition of a concentrated solution of potassium hydroxide caused the guanidine to separate as an oil, which soon solidified and was then filtered off. The yield was excellent.

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[1] Ber. d. chem. Ges., 12, 1002.

[2] Judging from the properties Feuerlein gives, the body he had was possibly the ammonium salt of phenylcyanamide.

Monophenylguanidine is soluble in water, alcohol, ether, warm chloroform, and warm benzene. Crystallized from the last solvent it melted at about 66°.[3] It decomposes on attempting to distil it in vacuo. The free base is hygroscopic and takes up carbon dioxide; for identification the chlorplatinate and benzoyl derivatives were prepared and analyzed.

Monophenylguanidine Chlorplatinate,[4] $(C_7H_9N_3)_2Pt_2Cl_6$.—Alcoholic solutions of monophenylguanidine and chlorplatinic

[3] Feuerlein could not have had monophenylguanidine, for he describes the body as exploding when heated.

[4] Feuerlein states that monophenylguanidine does not form a chlorplatinate.

Plaintiff's Exhibit No. 20 64

Plaintiff Exhibit No. 20-8/24/25-1915

CONSOLIDATION OF TABLES 1 AND 2 OF KRATZ'

PHILADELPHIA PAPER	AMOUNTS	PERCENT OR RUBBER	AMOUNTS CORRESPONDING TO 2% OF D.P.G. ON THE RUBBER	AMOUNTS CORRESPONDING TO 3% OF D.P.G. ON THE RUBBER
ANILINE	1.00	1.08	24.0	8.21
UREA	0.25	0.27	6.5	2.05
THIOUREA	0.30	0.324	7.8	2.46
MONO PHENYL THIOUREA	0.45	0.486	11.7	3.69
DI " " (THIOCARBANALIDE)	0.85	0.919	22.1	6.98
MONO PHENYL GUANIDINE	0.075	0.081	1.95	0.62
DI " "	0.075	0.081	1.95	0.62
TRI " "	0.30	0.54	13.0	4.10
ANHYDROFORMALDEHYDE ANILINE	0.75	0.81	11.25	6.28
p-PHENYLENE DIAMINE	0.17	0.183	4.42	1.40
MONOANHYDRO-FORMALDEHYDE p-PHENYLENE DIAMINE	0.14	0.151	3.64	1.15
DI " " " " "	0.14	0.151	3.64	1.15

FORMULA

RUBBER	92.5
SULFUR	7.5

KEUFFEL & ESSER CO., NEW YORK NO. 359 S.

	TABLE I	TABLE IV	
	% EQUIVALENT	% USED	COMBINED SULPHUR COEFFICIENT
ANILINE	1.00	.41	3.625
DIPHENYLTHIOUREA	.85	1.00	3.078
TRIPHENYL GUANIDINE	.50	1.25	3.872

Plaintiff's Exhibit No. 20 (Page 2)

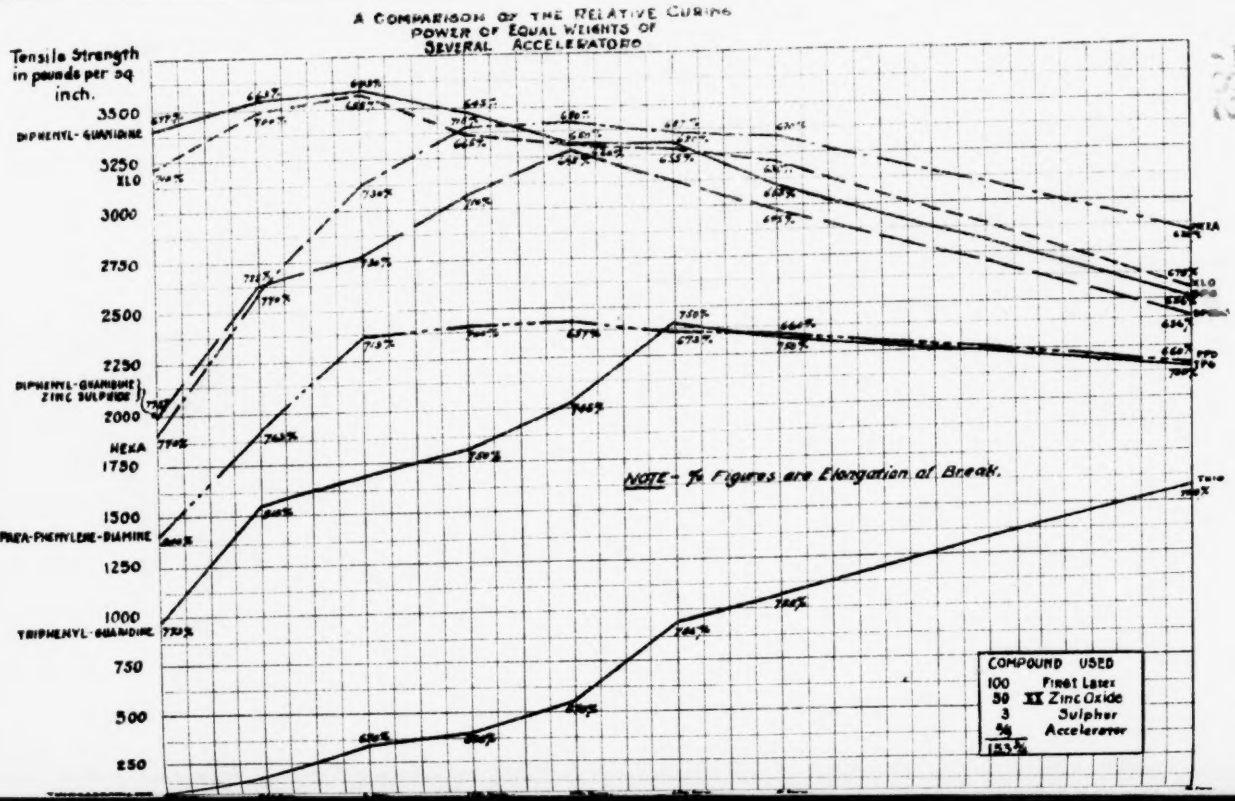
	Guanidine	DPG	TPG	Diorthotolyguanidine
	$NH:C(NH_2)(NH_2)$	$NH:C(NH\cdot C_6H_5)(NH\cdot C_6H_5)$	$C_6H_5N:C(NH\cdot C_6H_5)(NH\cdot C_6H_5)$	$NH:C(NH.NH_2)(NH_2)$
I	$CH_3NH.CS.SC_6H_5$	– a super-accelerator		
	$CH_3NH.CS.SC_6H_5$	– a very weak accelerator		
II	$CH_3(C_6H_5)N.CS.S_2.CS.N(CH_3)C_6H_5$	– a super-accelerator		
	$CH_3NH.CS.S_2.CS.NHCH_3$	– ~~practically~~ hardly any accelerating power		
III	$C_6H_5.NH.NH.C_6H_5$	– ~~retards~~ accelerates vulcanization		
	$C_6H_5NH.NH_2$	– retards "		
IV	$(CH_3)_2N.CS.S_2.CS.N(CH_3)_2$	– Tetramethyl Thiuram disulphide a super-accelerator		
	$CH_3N:C(SCH_3).S_2.C(SCH_3):NCH_3$	Tetramethyl Isothiuram disulphide		
	No accelerating action			
V	$CH_3CH(OH)NH_2$	– ~~no good~~ accelerator		
	$CH_2(CH_2OH)$	– not an accelerator		
VI	$OH.CH_2NH_2$	– an accelerator		
	$OH.C_6H_4$	– a retardant		

(Times, Review of Rubber, April 1920)

CHART SHOWING THAT THE INFLUENCE OF A CHANGE IN THE SUBSTITUTION CANNOT BE PREDICTED

Pfleiderer #31
Oct/25 "

Plaintiff's Exhibit No. 22



"6933.1"

The Effect of Organic Accelerators on the Vulcanization Coefficient.[1]

By D. F. Cranor.

A brief discussion of the already published work on the relationship of the mechanical properties of vulcanized rubber to the chemical composition, and a description of experiments with certain powerful accelerators which demonstrates that under certain conditions good mechanical properties can be obtained in rubber with a very low degree of chemical combination of sulphur

DURING THE PAST FEW YEARS considerable material has been published regarding the relationship of the mechanical properties to the chemical composition of vulcanized rubber. It has been demonstrated that if vulcanization is carried to a point where maximum physical properties are obtained in the freshly cured goods, such goods are overvulcanized and subject to rapid deterioration; also, that the proper degree of vulcanization for soft rubber can be accomplished with less chemical combination of sulphur in the case of quick curing stocks than with compounds which require prolonged heating to effect vulcanization. It is apparently quite generally believed that the coefficient of vulcanization for a properly cured pure gum mixing of good quality plantation *Hevea* rubber lies in the neighborhood of three; although it has been impossible to determine a coefficient which definitely represents the so-called optimum cure.

The fact that almost all practical rubber formulas to-day contain some one of the many organic accelerators makes further research necessary if scientific methods are to be applied to the estimation of the degree of cure of the mixings containing these substances. I have, therefore, undertaken extended work along these lines with view to making my testing methods more accurate and satisfactory. It has been the thought of the writer that results of greatest significance would be such as would indicate the amount of sulphur combination required to effect proper cure in a given sample of crude rubber, as compared with the combination necessary when the same rubber has added to it organic accelerators of various degrees of efficiency. Accordingly I have determined the physical properties and vulcanization coefficients of various samples of crude rubbers, when cured with and without accelerators, and have chosen certain series covering some of the results obtained in connection with powerful accelerators.

The determinations here described were made upon a mixing of standard rubber smoked sheet and a sample of inferior brown plantation crepe. In both cases 100 parts of rubber were mixed with 6 parts of sulphur and 1 of zinc oxide. The latter was included in order to have the compound workable to best advantage with accelerators which exert a maximum effect only when used in the presence of zinc oxide. The sulphur was set at 6 per cent on the weight of rubber, it being desired to use enough to get a stock capable of being overcured before showing the phenomena of reversion, which has been mentioned by Schidrowitz, and at the same time one in which the amount of sulphur is sufficiently low to obviate acceleration due to an excess, thus allowing the effect of the catalysts to be most clearly demonstrated. The percentage of zinc oxide is held at a maximum, it being used only to activate the accelerators added to these mixings. Even such an amount exerts a slight retarding action on the combination of sulphur, this having been proved by Van Heurn (See THE INDIA RUBBER WORLD, page 251, February 1 1919) and also by personal experience in our laboratory. This substance is also a factor in fixing the physical properties of the product, but it is necessary to include it in the basic formula in order to preserve the similarity of these mixtures with the treated compounds.

It will be noted by referring to Table I that the smoked sheet was vulcanized through a wide range of time changes at a vulcanizing temperature of 292 degrees F., or approximately forty-five pounds' steam pressure. All test specimens were cut by a die from sheets approximately 0.100 inch thick, which were vulcanized in an ordinary platen press, the temperature of which was controlled by a reducing valve. The tensile strength, ultimate elongation and loads required to produce definite elongations were determined by a Scott vertical combination rubber and fabric testing machine, the pulling jaw of which travels at a uniform rate of 20 inches per minute. The tensile product was calculated according to the method of Stevens. "Set" was determined in the case of the results recorded in Table I by stretching the specimen from one to eight inches and holding at such a setting for a period of ten minutes. The measurements were made ten minutes after releasing the samples from the jaws of the stretching device.

In the following tables the samples used for the "set" test were also stretched to eight inches, except in series where the figures for ultimate elongation are less than one to nine, in which case the samples for "set" were stretched from one to seven inches. As a matter of fact, practically no value is to be attached to the "set" results, as in many cases the figures are identical for samples having otherwise widely vary characteristics. They are inserted only to make the results complete, since the test is one which seems to be much used in general testing practice. The coefficient of vulcanization has in every instance been calculated from a direct determination of combined sulphur, made upon a sample extracted in acetone for a period of 24 hours at the boiling temperature of the solvent. The method used is the nitrate acid-bromine oxidation followed by fusion with potassium nitrate in presence of sodium carbonate. Two determinations were made upon each sample, and in almost every case the results check to within 0.10 per cent.

TABLE I.

COMPOUND A. UNTREATED SMOKED SHEET. PHYSICAL TEST VALUES AND COEFFICIENTS OF VULCANIZATION.

Minutes Curing at 292° F.	Tensile Strength Lbs. per Sq. In.	Set	Ultimate Elongation Inches	Tensile Product	Load 300% Elongation Lbs. per Sq. In.	Load 500% Elongation Lbs. per Sq. In.	Coefficient of Vulcanization
45	1616	1 to 9	8	1492	583	1060	1.23
100	1846	9	8	1519	570	1230	1.77
115	1788	9	8	1650	660	1215	2.01
130	1974	9	8	1713	700	1330	2.38
145	2213	9	7	2004	739	1515	2.95
160	2333	9	5	1948	749	1500	3.09
175	2029	9	3	1806	883	1740	4.36
190	2313	9	3	2134	950	1840	4.76
205	2251	9	3	2000	1040	2100	5.07
220	2400	9	3	2148	1005	2010	Broke
235	120	4.5	32	Broke	Broke	Broke	Broke

It is seen with the smoked sheet that the series commences with a "heat" quite insufficient for proper vulcanization, and continues through 15 minutes' time changes to cover the entire range, including under, good and overvulcanization, and finally in the case of the last two members of the series, reversion and degradation due to overheating after the free sulphur content has been reduced to less than 1 per cent. This is especially

[1] Read before the Rubber Division of the American Chemical Society at Philadelphia, Pennsylvania, September 5, 1919.

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appearance in the 235 minute cure which has a strength of 1,80 and an elongation of only 350 per cent or 1 to 4". Indeed, the ideal physical characteristics were to be taken as the maximum of strength, the 240-minute cure which shows the greatest tensile product, or the 305 minute which shows the greatest resistance to stretching would be selected. However, the former has a vulcanization coefficient of 4.75 and the latter of 5.07 and the author is confident that any rubber man would prefer either these pieces to be overvulcanized after making the usual commercial examination. Unfortunately insufficient time has elapsed since the original preparation of the samples to provide the results of natural weathering tests at this time. But accelerated aging tests if applied to an entire series such as this will show those members which are decidedly over or undercured and the results of physical and chemical tests made upon specimens so treated are therefore given in Table II.

TABLE II

Minutes Curing at 292° F.	Tensile Strength lbs. per sq. in.	Elongation %	Tensile Product	Load kgs. per sq. cm. at 500% Elong.	Set %	Coef. of Vulc.
120	1,611	700	1,127,700	12.5	5.0	
150	1,943	650	1,262,950	14.5	4.0	2.22
180	2,241	600	1,344,600	15.5	3.5	2.73
195	1,867	500	933,500	17.0	3.5	3.13
210			14,6	17.00	Broke	13.5
225			4.6	471	Broke	Broke
240			4.6	471	Broke	Broke
255			4.6	471	Broke	Broke
270	1,868	75	140,100	Broke	Broke	4.74
285	1,722	50	86,100	Broke	Broke	Broke
300	1,722	50	86,100	Broke	Broke	Broke
315	1,722	50	86,100	Broke	Broke	Broke
330			4.6	471	Broke	Broke
345			4.6	471	Broke	Broke
360			4.6	471	Broke	Broke

It is seen by the accelerated age test, that the sample cured 180 minutes having original vulcanization coefficient of 2.85 (Table I) is the best of the series. It will be noted that this cure yields sample having a maximum strength tensile product

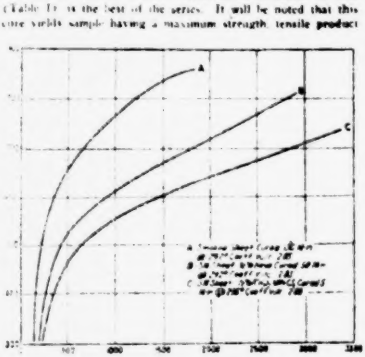

FIG. 1 STRESS-STRAIN CURVES

and the greatest resistance to stretching after the accelerated aging treatment. The selection of this as the best cured sample is well in accordance with the conclusions of Stevens in a paper read before the Society of Chemical Industry. In this it was shown that first-grade plantation rubbers vulcanized to a sulphur combination of about three stood up well during an aging period of 120 weeks, whereas those cured to a greater degree deteriorated quite rapidly. This same figure has been indicated as the proper coefficient for a mixing of the same in question by Spence, Kratz, Van Heurn and others.

Following the preparation and testing of the series mentioned, the accelerators monothiocarbanilide, diphenylguanidine, dimethyldiphenylethanamine, aldol addition product of dimethylamine and carbon bisulphide, were separately added to the original mixing, namely smoked sheet, 100 parts; sulphur 6 parts, zinc oxide 5 parts, in the proportion of 0.5 per cent to the rubber contained in the batch. The former was selected as a moderately active accelerator and the other as an example of a group which probably comprises the most active accelerators known and therefore one of the most valuable for use in illustrating the extreme possible effects of accelerators on the mechanical and chemical properties of the resulting vulcanizates. This relevance has been mentioned in the literature of rubber chemistry and should be a familiar one to our "Chemical Abstracts" January 10, 1916. The results in Table III show the effect of the aniline addition product in the mixing.

TABLE III

Minutes Curing at 292° F.	Tensile Strength lbs. per sq. in.	Elongation %	Tensile Product	Load kgs. per sq. cm. at 500% Elong.	Set %	Coef. of Vulc.
30	1,056	900	950,400	8.5	10.0	
60	1,346	900	1,211,400	11.0	12.5	1.39
90	2,000	900	1,800,000	15.5	10.0	2.07
120	2,013	850	1,711,050	17.0	7.5	2.32
150	2,240	800	1,792,000	18.5	7.5	2.58
180	2,136	750	1,602,000	19.0	7.5	2.85
210		700	1,470,000	19.5	7.5	3.04
240		650	1,365,000	20.0	7.5	3.42
270		600	1,260,000	20.5	7.5	3.80
300		550	1,155,000	21.0	7.5	4.18
330		500	1,050,000	21.5	7.5	4.56
360		450	945,000	22.0	7.5	4.94

It is apparent from these figures that the compound containing this substance not only cures in about one-third the time required for vulcanization of the untreated rubber in the same formula, but the relationship of mechanical properties to chemical composition is altogether altered. If we relate the physical properties to the vulcanization coefficient as standard, by comparing the 30-minute cure with coefficient of 2.85 with the 180-minute "correct" cure of the untreated smoked sheet at coefficient of 2.85 it is seen that the "hexa" stock has 1,044 pounds per square inch greater tensile strength, one half such its stretch, a tensile product higher by 824, and that more energy the load is required to stretch this stock to a given elongation. Making allowance for the toughening effect of the accelerator the "hexa" compound is somewhat overvulcanized at the 30-minute cure.

In Table IV are indicated the results obtained in using the dimethylamine addition product at a vulcanizing temperature of 292 degrees F.

TABLE IV

Minutes Curing at 292° F.	Tensile Strength lbs. per sq. in.	Elongation %	Tensile Product	Load kgs. per sq. cm. at 500% Elong.	Set %	Coef. of Vulc.
1	1,260	1,150	1,449,000	12.5	10.0	0.95
2	1,680	1,100	1,848,000	14.5	10.0	1.27
3	2,016	1,050	2,116,800	16.0	10.0	1.52
4	2,352	1,000	2,352,000	17.5	10.0	1.78
5	2,688	950	2,553,600	19.0	10.0	2.03
6	2,688	900	2,419,200	20.0	10.0	2.28
7	2,688	850	2,284,800	21.0	10.0	2.53
8	2,688	800	2,150,400	22.0	10.0	2.78
9	2,688	750	2,016,000	23.0	10.0	3.04
10	2,688	700	1,881,600	24.0	10.0	3.29
11	2,688	650	1,747,200	25.0	10.0	3.54
12	2,688	600	1,612,800	26.0	10.0	3.79
13	2,688	550	1,478,400	27.0	10.0	4.04
14	2,688	500	1,344,000	28.0	10.0	4.29
15	2,688	450	1,209,600	29.0	10.0	4.54

In this instance it is seen that samples having satisfactory physical properties were obtained in vulcanizing periods of three, four and five minutes with the abnormally low coefficients of 1.09, 1.21 and 1.45, respectively. The same mixture was also vulcanized at 295 degrees F., the results being given in Table V.

Plaintiff's Exhibit No. 23 (Page 2)

TABLE V

[illegible]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

Note: The greater degree of cure of this series as compared to that used in Table IV depends on factors introduced by the slight increase in temperature. It is probable that the raw stock was heated to a greater extent in the course of mixing.

In this series, the sample cured one minutes coefficient *2.00* closely approaches the *2.05* coefficient of the corresponding cured sample sheeted short. Comparing the physical characteristics of these two, we find a difference of 1,584 pounds tensile strength in favor of the accelerated stock, a loss of 1.2 inches in elongation at the breaking point, a tensile product higher by 927, and an even greater resistance to stretching than in the case of the rubber containing hexamethylene tetramine. This sample is undoubtedly much overvulcanized.

Figure 1 shows the stress-strain curves of the three samples, all taken from the same lot of rubber and all cured to vulcanization coefficients of 2.00 to 2.05 by means of vulcanizing periods ranging from five minutes to two hours and ten minutes. It affords a graphic illustration of the variation in physical properties referred to essentially the same vulcanization coefficient.

Figure 2, on the other hand, illustrates the range of the vulcanization coefficients for the same samples, referred to the load required to produce a uniform elongation of 700 per cent. By reference to these curves, we find that about 4.9 per cent of combined sulphur is necessary to produce a sample of unaged rubber requiring a load of 1,000 pounds to stretch it through 700 per cent. In the case of the same rubber containing in addition of ½ of one per cent of "hexa," the same effect was produced when about 1.8 per cent of sulphur has been combined. With the introduction of the dimethylamine addition product, the corresponding coefficient drops to 0.9 per cent. Figure 2 also exhibits a curve representing the compound reported in Table VI which consists of the basic formula and 1 per cent of the dimethylammonium-dimethyl-dithiocarbamate.

TABLE VI

[illegible]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

Sample cut with the grain
Sample cut across the grain
Sample cut with the grain
Sample cut across the grain

Three samples were not heated at all, being mixed, calendered and stored in the dark between sheets of holland cloth. The tests shown were made one month and two months after preparation, and certainly show that spontaneous vulcanization has taken place to a very considerable extent. With this mixing we find, since to a very considerable extent. With this unheated material would require the load of 1,000 pounds to stretch it to 700 per cent when only 0.7 per cent of sulphur has entered into combination with the rubber. The general tendency is for the curves to flatten toward the load axis as the period of heating is reduced, and this gives some indication of the extent to which rubber is depolymerized by heat and shows that extremely low sulphur combination is sufficient to vulcanize when the period of heating is reduced to a minimum or entirely omitted. The turn of the curve representing the unheated rubber in the neighborhood of the 5 per cent combined sulphur line again illustrated the reversion which takes place when heating is continued after the bulk of the sulphur has entered into combination. The turn at the 3 per cent point in the case of the "hexa" sample is indicative of the great care necessary when

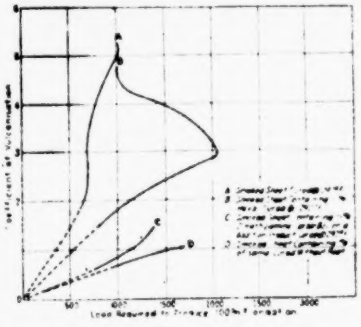

FIG 2. RANGE OF VULCANIZATION COEFFICIENT

using this substance, since if the sulphur in the compound is held down to a figure which is not low, results equally as disastrous as those coming from overcure will inevitably follow the overheating of such compounds.

Work along very similar lines was also carried out with an inferior type of brown plantation crepe, the results of which are indicated in Tables VII and VIII.

TABLE VII

[illegible]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

TABLE VIII

[illegible]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

In this case, the figures reported are limited to the tests made on the straight rubber and the same rubber to which was added ½ of 1 per cent of the dimethylamine-carbon bisulphide addition product. Preliminary tests on this rubber treated with hexamethylene tetramine showed that satisfactory vulcanization could only be obtained with the addition of higher proportions of zinc oxide. Figure 3 shows the complete stress-strain curves

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of 120, 180, 240 and 300-minute cures at 292 degrees F on the rubber with 6 per cent sulphur and 1 per cent zinc oxide, these being represented by the dotted line curves A, B, C and D, respectively. On the same graph there is also indicated the stress-strain curves corresponding to 1, 2, 3, 4 and 5-minute cures at 292 degrees F, in case of the same mixing containing a ½ of one per cent addition to the powerful catalyst, these being the solid lines E, F, G, H, J and K, respectively. Addition of ½ and ¼ of 1 per cent were not sufficient to produce good vulcanization at a temperature of 292 degrees in periods ranging from 2 to 5 minutes. These results are in general similar to those obtained by adding the accelerator to the smoked sheet, but are more notable, inasmuch as the brown crêpe was altogether incapable of being well vulcanized in its natural state, whereas through the use of the accelerator, samples having good physical properties are produced in extremely short vulcanizing periods.

It is to be noticed that the sample in Table VI cured 240 minutes and represented by Curve C in Figure 3, has all the characteristics of a technically undercured sample, although the coefficient amounts to 3.45, which is well above the 3 per cent limit mentioned for first-grade rubbers. On the other hand, the sample cured for 300 minutes is undoubtedly both overcured and overheated. The best cure would, therefore, fall between these points, but it is evident that no good cure is possible with this rubber except through treatment with chemical accelerating agents.

Although more results would be required before any definite conclusions should be drawn, the writer would summarize as follows:

SUMMARY.

(1) Although average good quality plantation *Hevea* rubbers may require a combination of sulphur of about 3 per cent to effect the proper or optimum cure, such rubbers can be vulcanized in a small fraction of the original time through the use of very powerful catalysts, together with zinc oxide, in which case excellent physical properties are obtained in samples, the vulcanization coefficient of which may be in the neighborhood of one.

(2) Inferior types of plantation rubbers which are incapable of being transformed into satisfactory vulcanizates through the

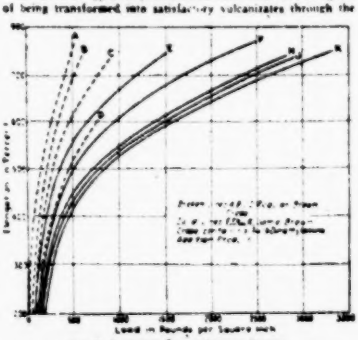


Fig. 3. Complete Stress-Strain Curves.

agency of sulphur alone may be readily vulcanized in very short curing periods and at normal vulcanizing temperatures through the use of powerful accelerators in the presence of small quantities of oxide of zinc. Although such rubbers may be undervulcanized when as much as 3½ per cent of sulphur is brought into combination through prolonged heating, good mechanical properties may be found in samples having abnormally low vulcanization coefficients when the vulcanization is carried out with maximum heating through the use of powerful accelerators.

(3) No definite figure can be established for the vulcanization coefficient of properly vulcanized soft rubber goods in general, or for the optimum cure of any mixing in particular, for the reason that the mechanical properties, as well as the chemical combination of sulphur is influenced by the time and degree of temperature used for vulcanizing.

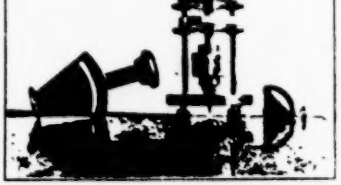
(4) It would appear probable, however, that in the case of any definite compound, the vulcanizing conditions could be standardized by the use of an accelerator and that the degree of vulcanization could then be checked most accurately through determinations of the coefficient of vulcanization.

SOME METHODS OF TESTING THE HARDNESS OF VULCANIZED RUBBER.

By H. P. Gurney.

USUAL QUALITATIVE METHODS.

The most natural way for an experienced rubber man to estimate the hardness of a piece of cured rubber is to note the force required to indent it with the point of a pencil or similarly convenient means. Although practical rubber workers are thus able to distinguish very accurately between different grades



Durometer. Plastometer. Durometer.

of rubber coverings, the information acquired is of no value as a matter of record since it cannot be designated quantitatively.

QUANTITATIVE METHODS.

Spring Type Apparatus. The use of any of these different instruments for obtaining a figure expressing the hardness of rubber surfaces affords an accurate method for the comparison and recording of the quality of hardness by an arbitrarily chosen number.

In instruments of the spring type, the force is applied by means of a spring and the rubber is indented by a point of specified shape and dimensions.

The Durometer is an extremely convenient pocket instrument of this class. On its scale the hardness of glass or steel registers 100, while that of soft rubber good may register as low as 40.

At the Boston Belting Corp.'s factory, a so-called "Durometer" has been in use for many years. This instrument is also of the spring type. A perfectly hard object has a durometer reading of 1000, while softer objects may run as low as 250. There is one marked disadvantage in the use of the spring type of hard-

[1] Read before the Rubber Division of the American Chemical Society, at the Philadelphia meeting, September 24, 1919.

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G. D. KRATZ.

TIRE AND METHOD OF MAKING SAME.

APPLICATION FILED MAY 26, 1919.

1,428,040. **Patented Sept. 5, 1922.**

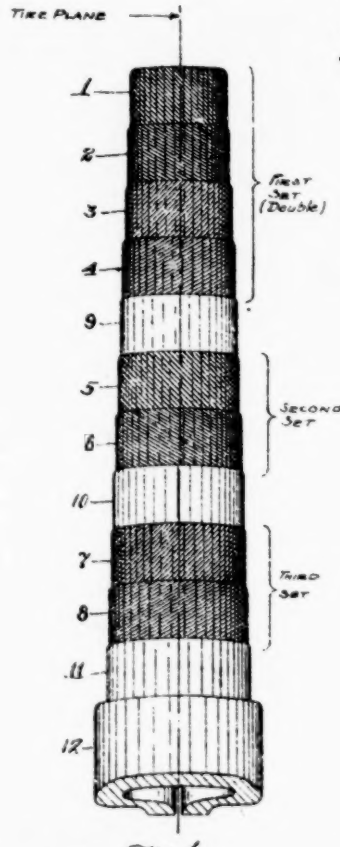

Fig. 1.

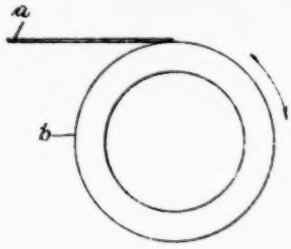

Fig. 3.

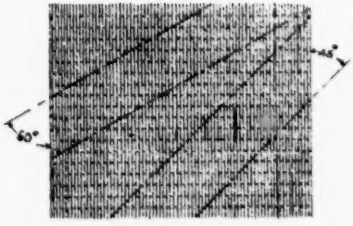

Fig. 2.

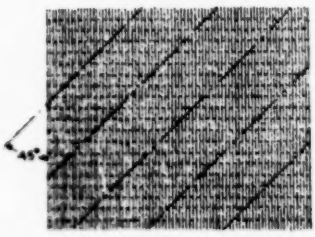

Fig. 4.

Fig. 5.

Fig. 6.

INVENTOR
George D. Kratz
By Jay Oberlin & Jay.
ATTORNEYS

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Patented Sept. 5, 1922. 1,428,040

UNITED STATES PATENT OFFICE.

GEORGE D. KRATZ, OF AKRON, OHIO, ASSIGNOR TO THE FALLS RUBBER COMPANY, OF CUYAHOGA FALLS, OHIO, A CORPORATION OF OHIO.

TIRE AND METHOD OF MAKING SAME.

Application filed May 26, 1919. Serial No. 299,575.

To all whom it may concern:

Be it known that I, GEORGE D. KRATZ, a citizen of the United States, and a resident of Akron, county of Summit, and State of Ohio, have invented a new and useful Improvement in Tires and Methods of Making Same, of which the following is a specification, the principle of the invention being herein explained and the best mode in which I have contemplated applying that principle, so as to distinguish it from other inventions.

The present improvements, relating, as indicated, to tires and methods of making same, have more particular regard to tire-shoes or casings, such as are largely used for motor-driven vehicles. More particularly still, such improvements relate to that type of tire-shoe which is constructed of so-called thread-fabric or cord fabric, i. e., of a fabric composed of strong longitudinal warp threads held together by fine non-strength-giving weft threads. In fact, in some cases such warp threads are held together simply by the film or coating of rubber which is ordinarily used as a cementing or binding material to hold the several layers of the tire together. In the present specification it will accordingly be understood that by the term "warp threads" such longitudinal strength-giving threads are referred to, irrespective of how they are held together.

Tires of the type in question have, so far as I am aware, been heretofore constructed in either one or the other of two ways. According to the first method of manufacture the layers of fabric, suitably rubber coated, as previously indicated, are applied one upon the other in such a manner that the warp threads of each layer of fabric are at right angles to the warp threads of each contiguous layer of fabric, whether above or below it. For example, in a six-ply thread fabric tire-shoe, constructed in accordance with this first method, the first, third and fifth layers of such fabric will have their threads parallel with each other and at an angle of 45 degrees to the plane of the tire, while the second, fourth and sixth layers will have their warp threads parallel with each other and at an angle of 45 degrees to the plane of the tire, but at right angles to the warp threads of the first-mentioned layers. The objection to this construction is that when the warp threads of contiguous layers or plies of fabric are thus at right angles to each other, even though they be separated by a rubber cushion, excessive friction occurs due to chafing between the crossed strands, and the heat generated by such friction is sufficient to materially weaken the tire carcass and to decrease the life of the same. A second method of construction of the type of tire in hand has consisted in applying a set of two, three or more contiguous layers of thread fabric with their respective warp threads parallel with each other and at an angle to the tire plane, and superimposing thereon another set of two, three or more layers of such fabric with their respective warp threads likewise parallel with each other, but disposed at an angle to the warp threads of the first set. By this construction the number of contacting or rubbing surfaces has been reduced, and it has also been considered that such construction can be more readily repaired than the first described construction, inasmuch as two plies of thread fabric can be removed together, thus permitting the introduction of new plies to replace them, which is next to impossible where such plies lie at right angles to each other.

Despite the foregoing points of superiority over the first described construction such second construction has nevertheless been found not entirely satisfactory. In the first place, the initial strength of a tire carcass constructed according to such second method is less than that of a similar carcass constructed according to the first method. In the second place, when a tire of such second construction is inflated the strands or threads in each layer are separated, i. e., the distance between individual strands in each layer is increased, owing to the fact that such layer is distended to cover a larger area, according to the pressure to which the tire is inflated, and to the extent to which pressure causes the carcass to distend. Accordingly, as the parallel strands in two contiguous layers are thus forced apart, there is a tendency for such strands in the one layer to fall into the interstices of the other, with the result that the effect of but a single layer of fabric is secured. Accordingly, in practice, this second construction amounts to but little more than the first, the several parallel layers of each group

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becoming, in effect, a single layer which is disposed at right angles to the parallel layers of the other group. The object of the present invention is to overcome the objections just noted as existing in connection with each of the two methods heretofore devised for the construction of fabric tires of the type in hand.

To the accomplishment of this object I apply the various layers of rubber-coated thread fabric in sets composed of two, three or more layers so cut or disposed that the strands of no two contiguous layers are either parallel or at right angles to each other. I accomplish this result, either by the use of plies of fabric which are cut on the bias, but at two or more different angles to the strands themselves, or by cutting all such plies on the bias at the same angle and subsequently distorting the individual plies as they are fixed in place in the carcass, so that their relative angles will be different. The invention, then, consists of the steps and means hereinafter fully described and particularly pointed out in the claims, the annexed drawing illustrating but one of several ways in which the principle of the invention may be utilized or embodied.

In such annexed drawing, Fig. 1 is a plan view of a section of a tire, shown for convenience as a straight, instead of a curved section, and with successive portions broken away, better to illustrate the interior construction thereof; Fig. 2 is a plan view showing a sheet of the thread fabric and the manner in which successive strips or plies are cut therefrom in order to construct the tire in accordance with the present invention; Fig. 3 is a side elevation, more or less diagrammatic in character, illustrating the manner in which such plies or layers of fabric are secured to the carcass; Fig. 4 is a view similar to Fig. 2, but shows another method of cutting the strips or plies from the sheet of fabric; Fig. 5 is a view of such a strip or ply; and Fig. 6 is a view of the same strip as in Fig. 5, but after it has been distorted or stretched to give the effect of the cutting of the same on a different angle from the original sheet.

In the illustrative construction of tire shown in Fig. 1, an eight-ply tire, or rather tire-shoe, is shown, the plies or layers of fabric being arranged in three sets, each made up of a plurality of contiguous layers or plies of thread fabric. The innermost of these sets, as shown at the upper end of the figure in question, is really a double set, being composed of four layers or plies, 1, 2, 3 and 4, the first such layer or ply being cut so that the strands therein lie at an angle of 45 degrees to the plane of the tire, and such layer being applied so that such strands run to the right of such plane; (that is, such strands lie at the angle and run in the direction stated with respect to a median circumferential line passing around the periphery of the tire, assuming such strip to be regarded from the outside of the tire and as being disposed in tangential relation thereto), the second layer or ply being cut at an angle of 30 degrees to the tire plane, and being applied so as to have the strands run to the right of such plane; the third layer or ply being cut at an angle of 45 degrees to the tire plane and being applied to have the strands run to the left of such plane; and the fourth layer or ply being cut at an angle of 30 degrees to the tire plane and being applied so as to have the strands run to the left of such plane. The relation of the various layers or threads in the layers comprising such set may be also described by stating that such layers or threads are at a slight angle to each other and diverge from each other at a median line at or parallel to the periphery of the tire, both threads lying in the quadrant formed by such a median line and a line at right angles to it passing through the point of intersection of said thread. The second set of contiguous layers of fabric comprises two such layers 5 and 6, the first of which is cut at an angle of 45 degrees to the tire plane and applied so as to have the strands run to the right of such plane, and the second of which is cut at an angle of 30 degrees and applied so as to have the strands run in the same direction as the first. The third set of contiguous layers of fabrics also comprises but two such layers 7 and 8, the first of which is cut at an angle of 45 degrees to the tire plane, but is then applied so as to have the strands run to the left of such plane, the second layer being cut at an angle of 30 degrees to the tire plane and applied so as to have the strands run in the same direction.

In between each successive set of such layers or plies of fabric there are preferably interposed layers 9 and 10 of rubber, respectively, which function in an insulating and cushioning capacity, but these rubber cushions are not essential. The outermost or last-mentioned set of layers of fabric is then covered by the usual breaker strip 11, which is composed of a heavy gum cushion of suitably prepared rubber calendered upon an open-weave fabric. Finally the whole is covered with an outer layer 12 of rubber constituting the tread of the tire.

Where the several strips, composing the successive sets of layers or plies of fabric, are initially cut from the original sheet of fabric upon the bias so that the strands therein will have the relative angularities described above, (see Fig. 2), the process of building my improved tire from these separate layers of fabric, rubber cushions and tread upon a solid or collapsible form

or core and then vulcanizing it, will be precisely the same as the method in current use in building tires, and need not, therefore, be further described. In Fig. 3 I illustrate diagrammatically the manner in which a strip *a* of fabric is applied to the core or carcass *b*, the arrow indicating the direction in which the core is intended to be rotated.

However, instead of thus initially cutting the several strips or layers of fabric in question so that the strands will lie at the desired angle, this involving a certain element of wastage, as will be indicated by an inspection of Fig. 2, I preferably cut these strips all in the same angle, thus reducing wastage to a minimum. Assuming the angle chosen to be 45 degrees, the typical strip *c* will then present the appearance illustrated in Fig. 5, which strip will obviously serve, without change, for half of the total number of strips required in the construction of the tire as just described, inasmuch as by simply reversing the strip, the strands *d* may be caused to run either to the right or left of the plane of the tire, as desired. In order to secure a different degree of angularity for the strands in the strip as applied from that to which the strip is thus initially cut, I then proceed as follows:— The strip cut as aforesaid, as later applied to the core or partially assembled carcass, is attached along its median line *e* only in the first instance. Then by pulling in opposite directions on the respective lateral edges of the strip, one such edge is applied in advance, and the other to the rear of its normal position, thus increasing or decreasing the angularity at which the strands lie to the plane of the tire. I have found it entirely feasible to change such angularity in this fashion from 45 degrees to 30 degrees, as illustrated in Fig. 6, for example, or reversely from 30 degrees to 45 degrees, and if preferred the strip may be distorted before it is applied.

Whichever method of construction is employed, it will be obvious that by arranging the superimposed layers or plies of fabric which compose the successive sets of such fabric, so that, while slightly divergent, the warp threads of said layers nevertheless run in the same direction (i. e., any two intersecting threads lie on the same side of a transverse line drawn through their points of intersection), I reduce the detrimental effects caused by the parallelism of strands in contiguous plies, and at the same time retain the greater portion of the initial strength obtained by crossing alternate and contiguous plies at right angles to each other. In other words, my method of superimposing plies of fabric, which have either been cut on the bias at two or more slightly divergent angles to the strands or threads, or else distorted or stretched to give the same effect, combines the advantages sought for in both of the two methods heretofore utilized, while at the same time I reduce the detrimental feature of chafing between the plies and its attending friction, which results in weakening the tire carcass. Finally, it will be seen that while my improved construction retains the carcass strength previously obtained by the first described prevailing construction, the added resiliency obtained by the second such construction has not been sacrificed.

Other modes of applying the principle of my invention may be employed instead of the one explained, change being made as regards the steps or mechanism herein disclosed, provided the means stated by any of the following claims or the equivalent of such stated means be employed.

I therefore particularly point out and distinctly claim as my invention:—

1. A component for a tire of the character described, comprising a set of superposed contiguous layers of thread fabric having their respective warp-threads lying at a slightly divergent angle to each other, but extending in the same general direction relative to a median line around the periphery of the tire, i. e. any two intersecting threads lie in the same quadrant formed by a transverse line and a line parallel with said median line passing through the point of intersection of said threads.

2. A tire of the character described, comprising a set of superposed contiguous layers of thread fabric having their respective warp-threads lying at a slightly divergent angle to each other but extending in the same general direction to the tire plane, i. e. any two intersecting threads lie in the same quadrant formed by a transverse line and a line parallel with said median line passing through the point of intersection of said threads, and another set of similar layers having their respective warp-threads also lying at a slightly divergent angle to each other, the warp-threads of said second set of layers similarly extending in the same general direction relatively to the tire plane but at an angle to the warp-threads of the first set of layers.

3. A tire of the character described, comprising a set of superposed contiguous layers of thread fabric having their respective warp-threads lying at a slightly divergent angle to each other but running in the same general direction relatively to the tire-plane, i. e. any two intersecting threads lie on the same side of a transverse line through their point of intersection, and another set of similar layers having their respective warp-threads also lying at a slightly divergent angle to each other, the warp-threads of said second set of layers similarly running in the same general direction

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relatively to the tire-plane but at an angle to the warp-threads of the first set of layers less than a right angle.

4. A tire of the character described, comprising a set of superposed contiguous layers of thread fabric having their respective warp-threads lying at a slightly divergent angle to each other, but running in the same general direction relatively to the tire-plane, i. e. any two intersecting threads lie in the same quadrant formed by a transverse line and a line parallel with a median line around the periphery of the tire passing through the point of intersection of such threads, another set of similar layers having their respective warp-threads also lying at a slightly divergent angle to each other, the warp-threads of such second set of layers similarly running in the same general direction relatively to the tire-plane but at an angle to the warp-threads of the first set of layers, and a layer of rubber forming a cushion between said two sets of fabric layers.

5. In a method of making tires of the character described, the steps which consist in applying circumferentially to a suitable mandrel a strip of fabric cut on the bias first along the median line of such strip and then retarding one edge only of such strip so as to modify the angularity of the component warp-threads therein relatively to the plane of such mandrel before fully applying such strip.

6. In a method of making tires of the character described, the steps which consist in applying circumferentially to a suitable mandrel a strip of fabric cut on the bias first along the median line of such strip and then pulling on the respective edges of said strip in opposite directions so as to modify the angularity of the component warp-threads therein relatively to the plane of such mandrel before fully applying such strip.

7. In a method of making tires of the character described, the steps which consist in applying circumferentially to a suitable mandrel successive strips of fabric on the bias, and distorting or stretching alternate such strips incidentally to application so as to vary the angularity of the component warp-threads from normal relatively to the plane of such mandrel.

Signed by me, this 23rd day of May, 1919.

GEORGE D. KRATZ.

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RUBBER AGE

FEBRUARY 25, 1929

The Action of Certain Organic Accelerators in the Vulcanization of Rubber—III

By G. D. Kratz, A. H. Flower and B. J. Shapiro

Falls Rubber Co., Cuyahoga Falls, Ohio

[illegible] that although aniline is effective as an accelerator in the absence of zinc oxide diphenylthiourea functions but feebly in the absence of, and strongly in the presence of, this substance. It remains to be added that [illegible] has been made indirectly in the literature quoted above and recently. These data have given curves for physical test results which demonstrate quite clearly the effectiveness of diphenylthiourea as an accelerator in the presence of zinc oxide. The statement that diphenylthiourea is practically inert in the absence of zinc oxide is, however, not in accord with our findings.

In a previous paper of this series we have shown that in the vulcanization of rubber with sulphur mixtures, [illegible] a definite part of diphenylthiourea is broken down into its constituent aromatic amine, but equal to that of one molecular part of aniline and one molecular part of [illegible] and

[illegible] which, however, were confined to the determination of the [illegible] at one rate only. In the present [illegible] we desired to compare the relative effects of [illegible] and diphenylthiourea over a series of cures, and to [illegible] the sulphur coefficients for the [illegible] mixtures and cures. Further it was desired to compare mixtures which contained [illegible] in addition to the rubber-sulphur mixture previously [illegible]

In the experimental part of this paper we have given results [illegible] for different cures, as follows: a rubber [illegible] which contained zinc oxide, and [illegible] which contained either one molecular part of [illegible] diphenylthiourea. All of the mixtures were vulcanized [illegible] at 274° F. [illegible] cures over a wide range of time. After [illegible] measurements of sulphur coefficients and physical properties were made.

Summary of Results

[illegible] briefly, we found that, in a rubber-sulphur mixture the accelerating effect of aniline is considerably greater than that of diphenylthiourea, when judged [illegible] by sulphur coefficients or on the basis of the physical

[illegible] of the Rubber Division of the American Chemical Society, Chicago, Ill., September 4 to 7, 1928.

[illegible] Ind. Eng. Chem., 21 (1929), 91.

[illegible] Rubber Chem. and Technology, 1 (1928), 377.

[illegible] Ind. Eng. Chem., 21 (1929), 911. In both cases the [illegible] is compared with aqueous soda as pointed out [illegible] Journal (3 (1928), 971).

When aniline is replaced by diphenylthiourea the reverse is true, and the activity of the original substance as an accelerator is greatly increased when measured by either the sulphur coefficients or physical properties. In the latter instances, then, the zinc oxide most probably either assists in the decomposition of the diphenylthiourea to a more active substance, or combines with the decomposition or alteration products or the original substance with the formation of a zinc salt, which is responsible

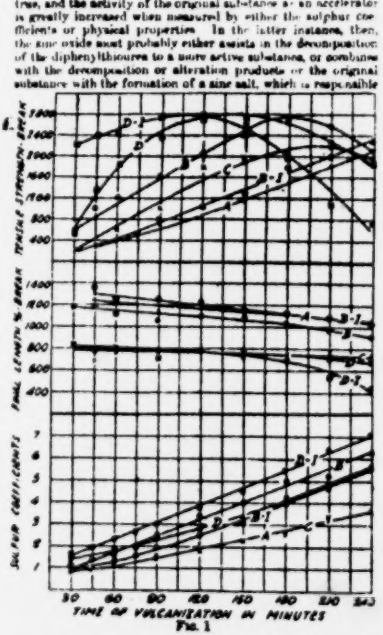

FIG. 1

for the increase both in the sulphur coefficients and tensile strength of the mixture. Our results with aniline as the accelerator, however, do not indicate the formation of such a salt.

Thus, in the presence of zinc oxide, the activity of aniline and diphenylthiourea as accelerators appears to be of different nature. Evidently, an acid substance, probably a thiocarbamic acid, capable of reacting with zinc oxide, is formed as one of the decomposition products of diphenylthiourea. The excess accelerating activity is attributed to this zinc salt. When aniline is employed as the accelerator, there is no evidence of such salt formation.

The present experiments were designed to effect a comparison of the sulphur coefficients and physical properties of representative mixtures when accelerated by 0.01 gram-molecular quantities of either aniline or diphenylthiourea. The six following mixtures were employed for this purpose, and each was vulcanized for a series of cures:

A—Rubber-sulphur control
B—Rubber, sulphur, and aniline
B-1—Rubber, sulphur, and diphenylthiourea
C—Rubber, sulphur, and zinc oxide control
D—Rubber, sulphur, zinc oxide, and aniline
D-1—Rubber, sulphur, zinc oxide, and diphenylthiourea

[1] Jour. Ind. & Eng. Chem., 12 (1920), 31.
[2] India Rubber World, 61 (1920), 356.
[3] In the experiments described in Parts I and II vulcanization was carried on at a temperature of 140° C.
[4] Satisfactory physical test results for compounding proportions obtainable with considerable difficulty. We found it necessary, particularly when making results for stress-strain diagrams, to employ three sets, one to operate the machine and two to take readings.
[5] As Whitby has stated ("Plantation Rubber and the Testing of Rubber," 1920, 206, Longmans, New York), complete stress-strain diagrams are probably required for an accurate determination of this point.

The quantities of each substance employed in these mixtures are shown in Table I. The amounts of aniline or diphenylthiourea added in these respective mixtures represent 0.01 gram-molecule of the accelerator per each 100 g. of rubber in the mixture. Otherwise, the same general method of procedure was adopted in the course of this work as in that previously reported in Part I.

The rubber used was of good quality, first latex, pale crepe, a different sample of the lot used in our former experiments. The various mixtures were mixed on the mill, vulcanized, and tested in the same manner as before. The physical properties of the vulcanized samples were determined on a Scott testing machine of the vertical type, with the jaws opening at the

TABLE I

Ingredient	Mix-ture A	Mix-ture B	Mix-ture C	Mix-ture D	Mix-ture B-1	Mix-ture D-1
Rubber	100.00	100.00	100.00	100.00	100.00	100.00
Zinc oxide			100.00	100.00		100.00
Sulphur	8.1	8.1	8.1	8.1	8.1	8.1
Aniline		0.93		0.93		
Diphenylthiourea					3.56	3.56

rate of 20 inches per minute. A recovery period of 48 hours was allowed before physical tests were made. Combined sulphur was estimated by our method previously reported in detail.[5]

The various mixtures were vulcanized at 141.8°C for different intervals of time up to 240 minutes.[4] The sulphur coefficients and physical properties of the different cures for each mixture were determined. These results are given in detail in Table II and shown graphically in Fig. 1. Generally speaking, the results obtained were in good agreement, and fairly smooth curves for physical properties were obtained.[4]

For brevity and clearness, the results obtained for each mixture have been considered separately.

The Results Obtained

MIXTURE A.—This mixture of rubber and sulphur served as a control only.

MIXTURE B—Comparing Curves A and B, aniline not only acts as an accelerator, but also slightly increases the physical properties of a rubber-sulphur mixture after vulcanization.

MIXTURE C—The inclusion of zinc oxide in Mixture C was found to have little or no effect upon the sulphur coefficients when compared with the results obtained for A.

MIXTURE D—The sulphur coefficients obtained for this mixture were found to be uniformly lower than the corresponding cures of B. Moreover, the maximum tensile strength of D was attained at a much lower sulphur coefficient than in the case of B, although this maximum tensile strength was almost the same in both instances.

MIXTURE B-1—From the curves it is seen that in a mixture of rubber and sulphur the activity of diphenylthiourea is much less than that of aniline, when judged by either sulphur coefficients or physical properties. In fact, both the tensile strengths and final lengths of B-1 are practically the same as those of its control mixture, A. The sulphur coefficients of B-1, however, were decidedly higher than those of A, and, contrary to the statement of Twiss, we cannot regard diphenylthiourea as practically inert as an accelerator in a mixture of rubber and sulphur only.

MIXTURE D-1—The sulphur coefficients for D-1 were considerably higher than those of any of the other mixtures; although the maximum tensile strength was of the same magnitude, it was reached in shorter time.

Comparison of Lengths

The curves showing the comparison of the final lengths are given in Fig. 1. It is obvious that the physical manifestations, especially in Mixtures D and D-1, are found in the tensile strength, rather than in the final lengths, of the vulcanized mixtures. Consequently, the tensile strengths of such mixtures, particularly until maximum tensile strength was reached, are better indications of the point known as the "optimum cure" than are the loads required to effect a given extension.[5]

The effect of the two accelerators, aniline and diphenylthiourea, have been summarized in Fig. 2, wherein with Mix

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Table II

All Mixtures Vulcanized at 141.5° C.

Time in Minutes	Mixture A			Mixture B			Mixture C			Mixture D			Mixture D-1			Mixture D-2		
	Sulphur Coefficient	Tensile Strength, Lbs. per Sq. In. at Break	Final Length at Break Per cent	Sulphur Coefficient	Tensile Strength, Lbs. per Sq. In. at Break	Final Length at Break Per cent	Sulphur Coefficient	Tensile Strength, Lbs. per Sq. In. at Break	Final Length at Break Per cent	Sulphur Coefficient	Tensile Strength, Lbs. per Sq. In. at Break	Final Length at Break Per cent	Sulphur Coefficient	Tensile Strength, Lbs. per Sq. In. at Break	Final Length at Break Per cent	Sulphur Coefficient	Tensile Strength, Lbs. per Sq. In. at Break	Final Length at Break Per cent
30	0.792			1.156	565	1140	1.005			1.484	560	710	0.833	375	1310	1.469	2310	920
45	0.858	278	1250	1.317	1010	1170	1.005	198	800	1.480	1380	770	1.063	475	1300	1.913	3201	780
60	1.018			1.583	1224	1130	1.207	362	750	1.459	1919	770	1.335	475	1300	2.207	3448	780
75	1.097	398	1220	1.686							1984	750	1.469	532	1280	2.423		
90	1.231	506	1180	2.002	1921	1140	1.558	1042	780	2.302	2302	750	1.868	799	1260	2.968	3720	790
135	2.108	972	1180	2.351	2046	1140	1.795	1615	760	2.401	2404	750	2.494	1055	1210	3.785	3889	770
150	2.726	1150	1130	2.733	2411	1140	2.317	1910	760	2.598	2521	770	3.100	1205	1150	4.531	3919	750
180	2.470	1751	1130	4.930	2972	1110	2.820	2193	740	4.229	2663	740	4.097	1779	1110	5.357	3793	690
210	3.179	1962	1100	5.274	3346	970	3.481	2146	740	4.666	2743	740	4.750	2021	1060	6.179	3118	530
240	3.751	2126	1060	6.244	2191	610	3.912	1976	720	5.194	1937	660	5.094	2163	1050	7.079	754	440

Test pieces 4.5 mm thick

tures A and C as controls, the excess sulphur coefficients were plotted against their times of vulcanization. A comparison of the curves for B and D show that, when judged by sulphur coefficients only, the activity of aniline as an accelerator is increased in the absence of zinc oxide. (3). On the other hand, a comparison of B-1 and D-1 shows that diphenylthiourea is approximately twice as active in the presence of zinc oxide than when this substance is absent from the mixture. In fact, the difference between curves B-1 and D-1 is so great that our results indicate the formation of a more and more active accelerator than the original diphenylthiourea, or its decomposition products. It is not permissible that the decomposition products of diphenylthiourea react with the zinc oxide in the presence of sulphur to form varying amounts of a zinc salt of a dithiocarbamic acid. Salts of the latter type have already been mentioned as violent accelerators. On the other hand, the fact that the curve for Mixture D, which contains aniline and zinc oxide, falls below that of B, which contains aniline but no zinc oxide, argues against the formation of diphenylthiourea and the subsequent formation of the zinc salt of its decomposition or conversion products from the aniline originally present in the mixture.

The preceding observations are probably applicable to mixtures of the same general type and composition as employed in the course of this work only.

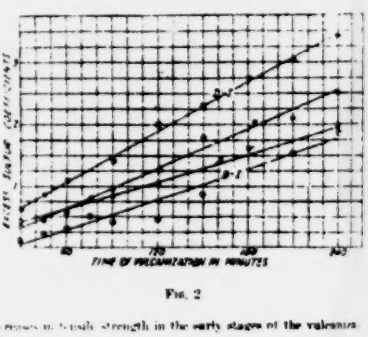

FIG. 2

Conclusions

(1). In a rubber sulphur mixture, the activity of aniline in the acceleration of vulcanization is much greater than that of a molecularly equivalent quantity of diphenylthiourea.

(2). In mixtures which contain zinc oxide, diphenylthiourea is more active than aniline.

(3). In mixtures accelerated by aniline, either with or without zinc oxide, the same maximum tensile strength is obtained.

The sulphur coefficients and physical properties of Mixture D are not concordant, but those of any of its other mixtures.

(4). Mixtures which contain zinc oxide, and which are accelerated by either aniline or diphenylthiourea, show large increases in tensile strength in the early stages of the vulcanization.

5. Mixtures which contain zinc oxide and which are accelerated by either aniline or diphenylthiourea, attain the same maximum tensile strength at approximately the same sulphur coefficients.

6. There is apparently no general relation between the physical properties and sulphur coefficients of accelerated mixtures.

Rubber Exports from Java

The exportation of plantation rubber from Java and Madoera amounted to 17,211 tons in 1918, as against 18,843 and 13,944 tons in 1917 and 1916, respectively. In 1918 Singapore imported 7,551 tons, as against 1,728 in 1917 and 2,077 in 1916. The United States, formerly the chief buyer, took but 5,844 tons in 1918, as against 14,840 tons in 1917 and 9,217 tons in 1916. From the outlying possessions the United States imported 7,640 tons in 1918, about one-half of the amount for 1917, which was 14,895 tons. Great Britain's trade likewise fell from 3,848 tons in 1917 to 1,895 tons in 1918. Singapore imports rose abruptly from 7,059 tons in 1917 to 16,485 tons in 1918. Considerable shipments were sent to Singapore, where the rubber was warehoused, awaiting a favorable opportunity for realization. The signing of the armistice restored favorable prices. 1 florin (40.482) per ½ kilo for prime qualities and 0.87½ florin (40.352) per ½ kilo for parcels containing 75 per cent of these qualities.

On November 15, 1918, the Rubber Producers' Union was formed at Batavia in order that united action might in the future be possible in marketing the colonial rubber.

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THE USE OF DIPHENYLGUANIDINE AS AN ACCELERATOR OF VULCANISATION.

By W. M. AMES, M.A., B.Sc.

Diphenylguanidine appears to be used to a very considerable extent by rubber manufacturers as an accelerator of vulcanisation, and a study of its properties as such may therefore be of value. There is now a large volume of literature dealing with the numerous organic accelerators, but practically all of it is concerned with the mechanism of the phenomenon of acceleration, and there is little information to assist the manufacturer in the actual use of these materials. In this respect diphenylguanidine, or, as it will be hereafter denoted for the sake of brevity, D.P.G., is no exception.

Kratz, Flower, and Coolidge (J. Ind. Eng. Chem., 1920, 12, 317) attempted to correlate chemical structure and accelerating effect for a number of substances, of which D.P.G. was one. They further gave data which showed it to be a very active material. Winfield Scott (India Rubber J., 1922, 64, 605) investigated some of its reactions, and (Ind. Eng. Chem., 1923, 15, 286) compared it with other guanidines in its behaviour towards sulphur. Regarding its technical use, Weber stated (India Rubber J., 1922, 63, 795) that it did not produce any discoloration in the finished article, that it could be incorporated without danger of premature vulcanisation in the mixing machine, and that quantities up to ½% on the rubber could be used with safety. It has been further stated (Le Caoutchouc et la Gutta Percha, 1923, 11816) that the most satisfactory quantity of sulphur to use along with it is from 3% to 5%, and that it produces very flat curing mixings. This rapid survey of the available literature on the subject indicates that the technical use of D.P.G. has perhaps not received the attention which has been given to such well-known organic accelerators as *p*-nitrosodimethylaniline, thiocarbanilide, and hexamethylenetetramine. In order to show how it compares in activity with some of the earlier discovered accelerators, the first portion of this paper is devoted to a comparison between D.P.G. and *p*-nitrosodimethylaniline, or "accelerene," as it is generally, for convenience, called.

This comparison was carried out first by vulcanising straight test pieces until they reached a standard elongation under a standard load, as indicated in an earlier paper (Anderson and Ames, J., 1923, 136T). Small equal quantities of D.P.G. and accelerene were incorporated into a control containing rubber and sulphur in the ratio 90:10. Another control containing, in addition, 5% of zinc oxide, had also small quantities of the accelerators added to it. In order to make the quantities of accelerator the same, allowance had to be made for the presence of 33% of water in the accelerene. The six mixings were thus made up as follows, figures denoting parts by weight:—(1) Control: Plantation sheet 90, sulphur 10. (2) Control 98, D.P.G. 2. (3) Control 98, accelerene 3. (4) Zinc oxide control: Plantation sheet 45, sulphur 5, zinc oxide 50. (5) Control (ZnO) 100, D.P.G. 1. (6) Control (ZnO) 100, accelerene 1½. The length of time at a temperature of 142° C. necessary to vulcanise test pieces made up with these mixings, so that they reached a standard elongation under a standard load, is shown in Table I. The acceleration is calculated as a percentage of the time of vulcanisation of the appropriate control.

TABLE I.

Mixing.	Time of vulcanisation at 142° C. (287° F.)	Acceleration %.
1	3 hr.	—
2	30 min.	89
3	15 „	92
4	2 hr.	—
5	15 min.	87
6	17 „	88

D.P.G. is seen to be an accelerator of practically the same power as accelerene. The presence of zinc oxide does not appear to have much effect on the activity of either, but that is really due to the defects of the method of investigation, which involves comparatively small extensions. Further, the mixings used are probably not suitable for the two accelerators concerned, though they are very useful generally for comparing different materials.

In order to provide a more reliable comparison between the two accelerators, they were incorporated into mixings of plantation sheet 100, sulphur 10, D.P.G. ½, and (A) zinc oxide 5 or (B) light magnesium carbonate 5. A^1 and B^1 are similar mixings containing accelerene, allowance again being made for the moisture present. The four mixings were vulcanised for various lengths of time in the form of slabs, from which ring test pieces were cut for testing on the Schopper machine. The results of these tests are shown in Table II.

TABLE II.

Mixing A. Time of vulc. at 142° C.	Breaking load kg./mm².	Final length, %.	Toughness 600% load, kg./mm².
1 hr.	1·44	847	0·41
¾ „	1·30	702	0·48
½ „	0·99	573	0·62
¼ „	0·43	502	0·73
Mixing A^1.			
20 min.	1·33	875	0·31
30 „	1·08	804	0·35
50 „	0·34	665	—
¼ hr.	0·25	605	—
Mixing B.			
30 min.	0·50	710	0·23
¾ hr.	0·95	948	0·24
1 „	0·88	908	0·30
Mixing B^1.			
15 min.	0·30	886	0·24
22 „	1·08	920	0·41
35 „	1·35	894	0·44

Comparison of the tensile figures for A and A^1 shows that, as far as strength is concerned, they are very similar. A^1 vulcanises slightly faster than A,

indicating that accelerene is the better accelerator of the two. It is noteworthy, however, that D.P.G. has a greater toughening effect than accelerene. The result of comparing B and B¹ is somewhat similar, except that the strength of the D.P.G. and magnesia mixing, B, is very poor.

From this preliminary investigation, then, it may be concluded that accelerene and the accelerator under consideration are not very different in activity; but it is also obvious that they are somewhat different in action.

In using such a substance the first necessity is to know the proportions of sulphur and accelerator which will give the most satisfactory results from the point of view of tensile properties, rate of cure, flatness of cure, toughness, and ageing. In the absence of any theoretical guidance, beyond very general statements, the only means of determining the optimum quantities of sulphur and accelerator is to adopt the method of trial and error, which was accordingly done.

To hard fine Para containing 5% of zinc oxide were added quantities of sulphur ranging from 1¼% to 15% of the rubber. To these different batches were again added quantities of D.P.G. ranging from ½% to 1% on the rubber, so that practically all possible combinations of sulphur and accelerator were investigated. The results are indicated in Table III.

1·5 [illegible] mixings
[illegible] cures at
142°.
Others at 135°

TABLE III

% Sulphur.	% D.P.G.	Time of vulcanisation at 135° C. Hr.	Breaking load. Kg. mm².	Final length. %	Toughness at 800% load Kg./mm².
1¼	½	¾	0·20	1062	0·09
		5/4	0·47	1071	0·16
		1	0·45	1060	0·12
		1¼	0·41	1093	0·11
		1½	0·37	1038	0·13
		1¾	0·33	1028	0·27
		2	0·81	1018	0·25
		2¼	0·87	994	0·29
		2½	0·73	999	0·23
		3	0·74	1040	0·22
1½	½	1	1·10	964	0·40
		1¼	1·04	967	0·42
		1½	1·30	956	0·49
		2	1·51	985	0·41
		2½	1·01	1007	0·34
2	0	¾	0·69	1063	0·18
		7	0·51	988	0·30
2	½	¾	0·31	1006	0·13
		¾	0·58	1056	0·15
		5	0·64	1016	0·24
		8	0·96	990	0·28
		10	0·44	927	0·22
2	¾	½	0·72	1008	0·26
		3	0·89	984	0·33
		¾	0·99	966	0·34
		4	1·03	900	0·38
		¾	0·96	940	0·35
2	¾	¾	0·78	991	0·29
		1¼	1·19	959	0·53
		1½	1·22	939	0·55
		2½	1·19	932	0·57
		2¾	1·31	927	0·65
2	1	¾	0·93	961	0·40
		1	1·27	927	0·62
		1¼	1·48	907	0·62
		1½	1·76	922	0·91
		1¾	1·72	897	1·04
5	0	¾	1·20	1036	0·34
5	½	¾	1·16	955	0·55
5	¾	¾	0·99	1034	0·22
		3	0·73	948	0·32
		4¼	0·96	972	0·38
		5¼	0·98	974	0·37
		6	0·94	914	0·47
5	¾	¾	0·69	981	0·42
		2¾	1·16	939	0·58
		3	1·31	934	0·63
		3¼	1·18	899	0·68
		7¼	1·23	923	0·84
5	¾	¾	1·32	969	0·58
		1¼	1·43	904	0·84
		1½	1·47	857	1·05
		2	1·43	865	0·96
		2¼	1·78	853	1·06
5	1	¾	1·40	946	0·70
		¾	1·63	901	0·99
		1	1·72	859	1·36
		1¼	1·72	821	1·54
		1½	1·80	815	1·69
7½	½	¾	1·31	978	0·50
		4	1·28	938	0·52
7½	¾	¾	0·55	997	0·21
		2¼	0·84	912	0·48
		3	1·06	922	0·56
		3¼	1·02	909	0·54
		4¼	0·91	965	0·38
7½	¾	¾	1·08	982	0·43
		1¼	1·05	922	0·68
		1½	1·23	936	0·62
		2	1·49	927	0·78
		2¼	1·67	843	0·83
		Min.			
7½	¾	¾	50	1·26	944	0·60
		Hr.			
		1¼	1·50	893	0·92
		1½	1·42	855	1·05
		1¾	1·53	794	1·41
		2	1·68	804	1·44
7½	1	¾	1·40	925	0·73
		1	1·66	870	1·18
		1¼	1·64	805	1·52
		1½	1·79	788	1·59
		1¾	2·13	787	2·24
10	½	¾	1·16	973	0·46
		2¼	1·18	955	0·52
		3	1·33	959	0·60
		3¼	1·56	930	0·57
		5¼	1·42	927	0·71
10	¾	¾	0·85	924	0·47
		1¼	0·89	923	0·45
		2	1·01	924	0·53
		2¼	1·15	939	0·59
		2¾	0·80	849	0·81
10	¾	¾	0·91	935	0·49
		1¼	1·21	893	0·77
		1½	1·18	856	0·87
		1¾	1·11	909	0·95
		2	1·02	813	0·90
10	¾	¾	1·13	855	0·83
		¾	1·41	876	0·97
		1¼	1·36	888	0·94
		1½	1·60	883	1·19
		2	0·93	713	1·34
10	1	¾	1·05	936	0·59
		¾	1·36	894	0·98
		¾	1·76	870	1·24
		1	1·48	799	1·66
		1¼	1·61	760	1·78
15	½	¾	0·99	925	0·54
		2¼	1·04	870	0·65
		2½	0·87	780	1·07
15	¾	¾	0·80	939	0·43
		1¼	0·79	894	0·62
		2	0·95	832	0·70
		2¼	0·81	823	0·70
		2½	0·44	871	0·34
15	¾	¾	1·20	925	0·66
		¾	1·18	883	0·78
		1¼	1·44	869	0·96
		1½	1·33	835	1·15
		2	0·84	720	1·31
15	¾	¾	1·23	918	0·71
		¾	1·45	881	1·00
		1	1·63	878	1·17
		1¼	1·35	791	1·45
		1½	0·78	810	1·74
15	1	¾	1·27	929	0·73
		¾	1·30	853	1·03
		¾	1·63	845	1·47
		1	1·84	777	1·86
		1¼	1·54	735	2·34

Hard fine Para was used throughout, in order to be reasonably certain of dealing with a normal rubber. The mixings were made up in each a way as to eliminate errors arising from slight deviations in the proper quantity of sulphur, and the rubber was mixed so that the amount required for the experiment would be as nearly uniform as possible. After the mixings had been prepared, they were heated over a range of cures in a "daylight" press, in the form of slabs. The time necessary being in some instances short, the heating was carried out at 135° C., except for the controls and for mixings containing 11½% of sulphur, which were heated at 142°. When the

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mixings had been vulcanised, ring test pieces were cut from the slabs and tested on the Schopper machine, giving the tensile data shown in Table III. Each observation of load and final length is the average of three readings. Before proceeding to general conclusions, the properties of each mixing are considered in detail.

No attempt was made to vulcanise a control mixing containing 1½% of sulphur. The addition of ½% of D.P.G. to such a mixing enables it to be properly vulcanised, although the tensile strength is very poor. It appears to be fully cured in about 3 hours at 142° C. Increasing the D.P.G. to ¾% improves the strength slightly, and reduces the time required to 2 hours. The third mixing of the series containing 1% of accelerator possesses quite good tensile strength, and is fully cured in 1½ hours. It is very noticeable that the addition of D.P.G. causes a marked increase in the toughness of the mixing, the increase becoming greater each time the accelerator is augmented. It appears probable that when these mixings are vulcanised beyond their maximum tensile point they become softer. This may be an indication of devulcanisation, due to prolonged heating in the presence of an active accelerator and a small quantity of sulphur.

In the case of the 3% sulphur mixings it was possible to compare the control with the accelerated mixings. The addition of ½% of D.P.G. to the stock makes practically no difference to its properties beyond reducing the time of vulcanisation, as indicated by the maximum strength, from 12 hours to 8 hours at 135° C. Further increase in the quantity of accelerator up to ¾% ensures an increase in both strength and toughness, and brings about a reduction in the time of vulcanisation to 4 hours. The ½% and 1% mixings show a very decided improvement in tensile properties. The toughness of each mixing increases with the addition of D.P.G., and in both cases flat curing properties are beginning to be evident. The strength attained by the last of the 3% sulphur series is noteworthy when considered alone, and is outstanding when contrasted with that of the control.

The same features may be noticed by referring to the tensile figures for the 5% and 7½% sulphur mixings. The various effects, however, are becoming very much intensified with increase in the quantity of sulphur. The only exception to this is that in the case of the two mixings containing only ½% of accelerator, the tensile strength is less than that of the control. The 7½% sulphur mixing with 1% of D.P.G. gives a strength of 2·13 kg. per sq. mm.

The 10% and 15% sulphur mixings represent a retrogression. They do not reach the same strength or toughness as the previous mixing, although there is a slight increase in acceleration. Reduction in strength with the addition of small quantities of D.P.G. is again noticeable. In spite of the retrograde movement with respect to tensile properties, both series of mixings are still satisfactory as regards strength, especially those containing larger quantities of accelerator.

In order to demonstrate the general features of D.P.G. as an accelerator, and to indicate clearly the type of mixing in which it should be used, a series of diagrams have been made. Fig. 1 shows how the maximum load obtained over the range of cures

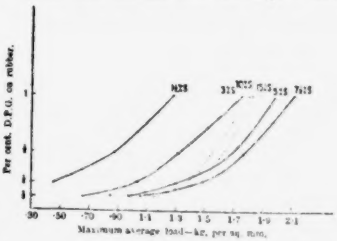

FIG. 1.

behaves with different quantities of accelerator in mixings containing different quantities of sulphur. After the points on this diagram had been plotted, it was found that they lay on a series of curves which corresponded to the different proportions of sulphur. This is the case, also, for the other diagrams, except for Fig. 4, which is an indication that the quantity of sulphur present is one of the main factors determining the properties of an accelerated mixing. Reverting to Fig. 1, it is clear that for every mixing, increase in the quantity of D.P.G. produces an increase in strength, the increment being greater when the quantity of accelerator present is small than when it is already large. As sulphur is added up to 7½%, the curves move further away from the D.P.G. axis and do not intersect, showing that the breaking load becomes greater as the proportion of sulphur is increased, no matter what quantity of accelerator is present. The 10% and 15% curves

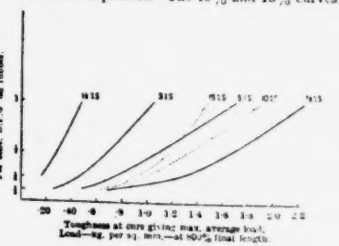
Per cent. D.P.G. on rubber.
1
¾
½
¼
·20 ·40 ·6 ·8 1·0 1·2 1·4 1·6 1·8 2·0 2·2
Toughness at cure giving max. average load.
Load—kg. per sq. mm.—at 800% final length.

FIG. 2.

lie, however, nearer the vertical axis, which indicates that for all quantities of D.P.G., adding sulphur beyond 7½% causes the strength to decrease. This result cannot be due to the addition of sulphur alone, for a 10% sulphur mixing containing no accelerator possesses a better tensile strength than

one containing 7½%; it must therefore be due to the sulphur and D.P.G. together.

Fig. 2 shows the relation between the toughness (measured by the load required to produce a final length of 800%) of the mixings when they are at their maximum strength, and the quantity of accelerator present, for the different proportions of sulphur. This is thus a comparison of the toughness of the mixings under similar conditions of cure. As noted above, points when plotted lie on curves corresponding to the proportion of sulphur in the mixing. Further, however, for small quantities of sulphur the curves are straight lines, showing that the additional toughness due to the accelerator is practically proportional to the quantity of D.P.G. present. For all the curves the toughening effect increases with the addition of accelerator. When the amount of sulphur present is large, the increase is greatest when the proportion of D.P.G. is small. As regards their position relative to the D.P.G. axis, the curves on Fig. 2 are similar to those on Fig. 1, the toughening effect increasing for all quantities of D.P.G. up to 7½% sulphur and diminishing for quantities of sulphur greater than that. Toughness and strength thus vary similarly in mixings accelerated with D.P.G.

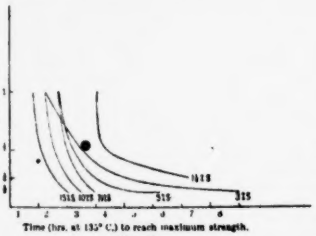

FIG. 3.

Fig. 3 shows the time (at 133° C.) required to reach the maximum strength, plotted against quantity of accelerator. Again, curves for the different proportions of sulphur can be drawn. Their position with respect to the D.P.G. axis indicates that as the quantity of sulphur is augmented, the time of cure is reduced, and there is no break in the continuity of this law at the 7½% curve. From 1½% to 15% sulphur the curves gradually approach the vertical axis. The portions of the curves above the ½% line are practically parallel to the D.P.G. axis, indicating that there is almost no increase in acceleration when more than ½% of D.P.G. is added. The acceleration is produced greatest with small quantities of sulphur, and the lower part of the curves being almost parallel to the time axis, the maximum increase in acceleration is obtained with proportions of accelerator less than ½%. The slope of the lower part of the curves gradually diminishes as sulphur is added, so that for large proportions of sulphur a small quantity of D.P.G. is almost as effective in reducing the time of cure as a large quantity.

An attempt has been made in Fig. 4 to show that when use is made of an accelerator, certain limitations are imposed in order that the good qualities imparted by such a material may be utilised to their fullest extent. The three properties which are most likely to require consideration in producing a new mixing are time of vulcanisation, strength, and toughness. Fig. 4 shows maximum strength plotted against the

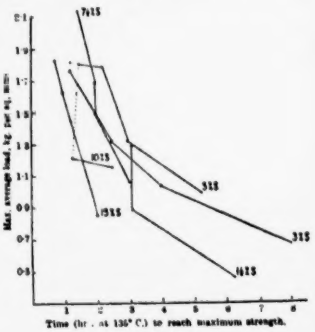

FIG. 4.

time (at 135° C.) required for its development. A similar diagram could be drawn for toughness. For convenience in identification purposes points representing mixings containing the same quantity of sulphur have been connected up. It will be observed that the majority of the mixings reach their best strength between 1 hour and 3 hours at 135° C. A few of very low strength take longer. This indicates that if a mixing is to be produced containing D.P.G. possessing good tensile properties, other circumstances must be such that it can be heated for about 1 hour at 135° C. subject to the influence of the compounding ingredients used. A similar diagram for toughness is not shown here, but it should be noted that satisfactory mixings containing D.P.G. will have certain definite limits of toughness between which they will lie, again subject to the effect of other ingredients. This is very important technically, as it indicates that radical alterations may have to be made in the compounding ingredients of a technical mixing when this accelerator is added in order that the accelerated mixing may possess exactly similar properties to the original, or conform to some specification. In some cases it is conceivable that the use of D.P.G. may be impossible.

Hitherto, in discussing the results, it has been assumed that the time taken to reach the maximum strength indicated when the mixings were fully

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vulcanised. In Table IV. are given times of vulcanisation which are considered suitable for technical work, together with the strength developed.

TABLE IV.

% Sulphur.	% D.P.G.	Time of vulcanisation at 135° C. Hrs.	Strength, kg/mm².
1½	½	0	0·42
	1	3	0·88
	2	3	1·28
2	½	3½	0·58
	1	3	0·99
	2	2	1·22
	3	1	1·48
3	½	2	0·73
	1	1½	1·18
	2	1	1·43
	3	¾	1·41
4½	½	2½	0·94
	1	1½	1·29
	2	1	1·50
	3	¾	1·60
10	½	2½	1·01
	1	1½	1·18
	2	1	1·41
	3	¾	1·36
15	½	2	0·85
	1	1½	1·44
	2	¾	1·45
	3	½	1·30

These have been arrived at by taking the first cure giving a reasonably good strength. In most cases the maximum strength is not reached until the mixing has been heated for a considerably longer period, and in all instances except for a few mixings containing a small quantity of sulphur or a small quantity of accelerator, there is a long range of time over which good tensile properties may be obtained. For technical work, therefore, most of the above mixings possess a very big margin of safety. Reference to Table III. shows that this accelerator produces mixings which are very much flatter curing than the controls. This must be reckoned as one of the most valuable properties of D.P.G.

From the above investigation it may be concluded that the best type of mixing to use with this accelerator is one in which the quantity of sulphur is in the neighbourhood of 7½% of the rubber, and the accelerator approximately ½% of the rubber. The quantity of sulphur necessary to bring out the full effect of D.P.G. is thus rather in excess of what might have been expected.

Hitherto, this work has dealt with mixings which are practically pure, containing only sufficient zinc oxide to activate the D.P.G. The possibility arises, however, that the conclusions may not be valid for compounded mixings particularly when active ingredients are present. As it is certain that if the presence of active fillers does not invalidate the previous results, inactive fillers will not, it is sufficient to investigate how D.P.G. behaves in mixings containing large quantities of zinc oxide and light magnesium carbonate. Litharge is not considered, as it is such a good accelerator by itself that it does not appear necessary or advisable that it should be used along with a powerful organic accelerator. Accordingly, the next portion of the experimental work dealt with mixings containing large quantities of zinc oxide and of light magnesium carbonate. In order to reduce the work necessary to a manageable amount, four representative mixings were chosen in such a way that the conclusions from their behaviour would be general for any combination of accelerator and sulphur. Two of the mixings contained a large quantity of sulphur with large and small quantities of D.P.G. respectively. The other two mixings contained a small quantity of sulphur with large and small quantities of D.P.G. respectively. Again, instead of adding different amounts of filler to these control mixings, the largest quantity of zinc oxide and of magnesia which can be efficiently used in rubber, was fixed upon as a suitable quantity to investigate. This procedure is justifiable in that addition of these substances up to that amount causes a progressive change in the physical characteristics of the rubber, and maximum effects were therefore being investigated. The actual quantity of filler which was added, namely 30% of zinc oxide, and 15% of light magnesium carbonate, had already been determined in previous experiments, and is in accordance with that indicated by Wiegand (India Rubber J., 1920, 60, 423).

Each mixing was cured over a range so as to exhibit the maximum tensile properties, and ring test pieces from each heat were tested on the Schopper machine. The resulting tensile figures are shown in Table V. For convenience the tensile figures for the controls have been abstracted from Table III., and are shown alongside those of the corresponding zinc and magnesia mixings. The figures given in the table are again average values obtained by breaking three rings.

TABLE V.

Cure at 275°F.	Rubber 100, sulphur 7½, D.P.G. 1. With 5% zinc oxide. Load. kg./mm.²	Final length. %	Tough-ness load. kg./mm.²	With 30% zinc oxide. Load. kg./mm.²	Final length. %	Tough-ness load. kg./mm.²	With 5% zinc oxide and 15% light magnesium carbonate. Load. kg./mm.²	Final length. %	Tough-ness load. kg./mm.²
¼	—	—	—	—	—	—	1·33	807	0·79
½	1·40	925	0·41	—	—	—	1·61	793	1·28
¾	1·60	870	0·59	1·61	844	0·77	1·66	721	1·83
1	1·64	805	0·67	1·63	833	0·83	2·05	720	1·87
1½	1·79	788	1·01	1·64	810	1·09	2·10	694	2·16
2	2·13	787	1·31	1·66	786	1·26	—	—	—
2½	—	—	—	1·60	777	1·38	1·70	690	1·48
3	—	—	—	1·48	874	1·08	—	—	—
	Rubber 100, sulphur 7½, D.P.G. ½%.								
1½	0·55	987	0·13	—	—	—	—	—	—
2½	0·94	912	0·27	0·81	874	0·35	1·30	828	0·48
3	1·06	923	0·36	0·74	829	0·40	1·61	807	0·74
3½	—	—	—	—	—	—	1·60	882	0·61
4	1·02	909	0·30	0·86	747	0·41	1·43	843	0·79
4	—	—	—	0·85	789	0·49	1·30	843	0·89
4½	0·91	883	0·38	0·81	861	0·44	1·51	832	0·90
5	—	—	—	0·72	739	0·52	—	—	—
	Rubber 100, sulphur 3, D.P.G. 1.								
½	0·93	961	0·22	—	—	—	1·37	822	0·84
1	1·37	934	0·35	—	—	—	1·64	784	1·15
1	1·48	867	0·45	1·23	870	0·52	1·61	764	1·41
1½	1·76	922	0·48	—	—	—	1·75	790	1·38
1½	1·73	907	0·45	1·42	883	0·43	1·66	785	1·49
2	—	—	—	1·49	851	0·77	2·00	739	1·69
2½	—	—	—	1·54	830	0·88	—	—	—
2½	—	—	—	1·75	833	0·95	—	—	—
3	—	—	—	1·60	791	0·91	—	—	—
	Rubber 100, sulphur 3, D.P.G. ½.								
2	0·21	1000	0·09	—	—	—	—	—	—
2½	0·58	1056	0·10	—	—	—	—	—	—
3	0·44	1013	0·12	—	—	—	—	—	—
6	—	—	—	0·29	730	0·24	0·43	747	0·33
7	—	—	—	0·50	949	0·24	0·61	804	0·31
8	0·64	990	0·18	0·57	891	0·23	0·67	885	0·27
9	—	—	—	0·56	891	0·23	0·60	848	0·26
10	0·44	997	0·15	0·19	884	0·22	0·45	880	0·21

With mixings containing a large quantity of sulphur and 1% of accelerator, the addition of zinc oxide causes a reduction in strength, and also probably slows down the rate of vulcanisation. It produces, however, a slightly tougher rubber, this effect being

rather more marked at an advanced state of cure. The addition of magnesia to the mixing decidedly improves its qualities. Increased strength is obtained from a rubber already outstanding in this respect, coupled with a considerable increase in toughness, rendering the magnesia mixing superior to the zinc mixing. The addition of magnesia also appears to produce further acceleration in the rate of vulcanisation.

Similar effects are noticeable with mixings containing a large quantity of sulphur and a small quantity of D.P.G. The control mixing in this instance—not a particularly good one in respect of tensile properties—is not improved by the addition of zinc oxide. The strength shows a distinct tendency to drop. The maximum strength is not attained until 4½ hrs., as against 3 hrs. for the control. The only improvement effected by the addition is a slight increase in toughness. Very different is the action of the magnesia. The strength is very much increased, and the rate of cure of the control not only maintained, but probably slightly increased. Again, there is a great increase in toughness. Perhaps the most remarkable feature of this magnesia mixing is its flat-curing property. The strength remains good from 2½ to 4½ hrs., and though the mixing is gradually increasing in toughness the increase is not great. The other magnesia mixing possessed the same flat-curing properties as regards strength, but not as regards toughness.

Mag. cont. mixing is flat curing

The mixings containing a small quantity of sulphur with a large quantity of accelerator show the effects due to the addition of the two fillers better than any others. The addition of zinc oxide in this case produces practically no alteration in strength, and there is a slight increase in toughness. The rate of cure, however, is slowed down very considerably, the increase in the time required to reach the maximum strength being 1½ hrs. on an original heat of 1½ hrs., or 100%. The zinc oxide mixing shows rather a long range of cures which give good strength. The action of the magnesia is very marked. There is an increase in strength, coupled with a slight increase in the rate of cure. A very great toughening effect is produced. In respect of strength the mixing is very flat curing. In general qualities this magnesia mixing is very much superior to the corresponding zinc one.

The last lot of mixings containing a small quantity of sulphur along with a small quantity of D.P.G. is very disappointing. The control in this instance has poor tensile properties, and the addition of fillers does not improve matters. Both zinc oxide and magnesia seem to slow down the rate of vulcanisation of the already slow-curing control.

Considering these results generally, it is evident that the effects produced by the addition of zinc oxide to a mixing accelerated with D.P.G. are not very desirable. Firstly, no increase in strength is produced, there being in fact a slight diminution, which; however, is negligible, particularly as the accelerated mixings are usually very strong. The toughening effect is less than would have been expected. That is, the zinc oxide has a smaller effect on the accelerated mixing—which has already been toughened—than it has when no accelerator is present. The magnitude of the toughness induced by zinc oxide varies with different types of mixings, increasing as the sulphur decreases or with decrease in the quantity of accelerator. It is a well-known fact that the addition of an active filler to a mixing already containing another active filler produces less increase in toughness than if the second filler had been added to a pure stock. In the case under consideration, sulphur and accelerator behave as if they were equivalent to an active filler, so that the full benefit of the toughening powers of the zinc oxide is not obtained. Another disadvantage of using D.P.G. in zinc oxide mixings is the reduction in the rate of cure produced by so doing. This retarding effect of the zinc oxide is greatest when the quantities of accelerator and sulphur present are small. It can be shown that zinc oxide alone has no effect on the time of cure as measured by the time taken to reach maximum strength, so that the retardation noted above must be due to the zinc oxide and D.P.G. conjointly. It is, in fact, a reversal of the activation process. The activity of D.P.G. must be brought up to a maximum by the addition of zinc oxide and then slowly reduced. The magnitude of such an effect would obviously be influenced by the amount of sulphur and accelerator present, and, in particular, it would be greater with small amounts of accelerator. From the behaviour of the mixings investigated, it is concluded that D.P.G. should not be used in zinc oxide mixings unless it is permissible to have present as much as 1% of D.P.G. on the rubber along with a fairly high sulphur content.

The general effects of the addition of light magnesium carbonate to D.P.G. mixings are very different. For all mixings except when accelerator and sulphur are both present in small quantities, the addition of magnesia produces an increase in strength, an increase in the rate of cure, and a toughening effect very similar to what would be obtained if no accelerator had originally been present. The increased strength is most marked when a small quantity of accelerator is used along with a large quantity of sulphur. The augmented toughness is perhaps most marked with a small quantity of sulphur and a large quantity of accelerator. Although it fails to effect any improvement in mixings where both the sulphur and accelerator content are low, the mixings examined above are sufficient to show that in magnesia mixings the good properties of this accelerator are exhibited to their fullest degree.

Hitherto, nothing has been encountered which would indicate that as an accelerator D.P.G. behaves any less efficiently in compounded mixings than in mixings containing nothing but rubber, sulphur, and sufficient zinc oxide to activate it. However, in making experiments with accelerated mixings containing brown rubber substitute, considerable trouble was experienced due to porosity. It has since been noted (Lefebure, India Rubber J., 1923, 66, 932) that D.P.G. does not give good results with mixings containing white substitute. To investigate this

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matter, a control (113½ pts.) consisting of hard fine Para 100, zinc oxide 5, sulphur 7½, and D.P.G. 1, was tested alone and with increasing quantities of brown substitute as shown in Table VI. The control and the first four mixings were heated in an autoclave press in the form of slabs for ¾ hr. at 135° C. The last mixing was heated in the same way for 1 hr. at 142° C. In none of the samples could any signs of porosity be detected.

TABLE VI.

Mixing.	Cure	Load. kg./mm².	Final length. %	Toughness 700% load. kg./mm².
Control ..	½ hr. ..	1·80 ..	344 ..	1·47
17½ Sub. ..	½ „ ..	1·71 ..	346 ..	1·38
25 „ ..	½ „ ..	1·70 ..	336 ..	1·34
35 „ ..	½ „ ..	1·68 ..	331 ..	1·36
40 „ ..	½ „ ..	1·62 ..	338 ..	1·03
40 „ .. *	1 „ ..	0·80 ..	671 ..	—

* With additional 5% of light magnesium carbonate.

As might have been expected, with increase in the quantity of substitute the strength diminishes. The mixings also become rapidly softer, and that may be taken as an indication of the rate of cure being slowed down as the substitute is increased. Magnesia was added to the last mixing in the hope that it would effect an improvement. The reverse is the case. The porosity encountered in mixings of this type is probably due to the slowing down of the rate of cure. From these results it would appear that D.P.G. should not be used along with mixings containing brown substitute. Although figures are not given, the same conclusion applies to white substitute. Probably the reason for this incompatibility of substitutes and accelerator is to be found in the traces of acid always present in these materials

Another factor which requires consideration when an accelerator is added to a mixing is its influence, if any, upon the ageing properties of the rubber. There has, perhaps, always been some suspicion that rubber containing accelerators is liable to perish more rapidly than ordinary mixings. This point was investigated for D.P.G. by subjecting two of the mixings to an artificial ageing test in an oven. As there is a general similarity in behaviour amongst the mixings dealt with, the choice of two, as being sufficient to indicate the ageing qualities of D.P.G. mixings in general, seems legitimate. The mixings chosen contained large and small quantities of sulphur respectively, with enough D.P.G. in each case to ensure that the mixings would possess reasonably good strength when properly cured, and would also be fairly fast curing. Both mixings contained hard fine Para 100, and zinc oxide 5, whilst A contained in addition 7½ pts. of sulphur and ½ of D.P.G., and B 3 of sulphur 1 of D.P.G. Large batches of A and B were mixed, and sufficient of both vulcanised to provide 55 rings for testing on the Schopper machine. Each mixing was vulcanised for two different times, one of which was supposed to be below that giving the optimum tensile figures, while the other was supposed to be that giving the maximum strength. However, the heats for A turned out to be rather long, and both are actually over-cures. In order to eliminate errors in vulcanisation, as many slabs of each mixing were heated together as practical difficulties would allow. After curing, five rings of each heat were tested, and the remainder of the slabs put into a ventilated oven which was automatically kept at a temperature of 70° C. Each day after this slabs were removed, allowed to cool, and tested. Tensile figures for every second day are shown in Table VII., readings representing averages being obtained by breaking 5 rings.

With mixing A the loads obtained for both cures gradually diminish from the start, which shows that it has been over-cured. In spite of this the load shows no sudden decrease until the 10th day. This is better than the usual behaviour of rubber-sulphur mixings. The strength remains quite noteworthy for 6 days. As the rubber ages there is a gradual increase in toughness, but not as much as might have been expected. The longer cure represents a rather bad over-cure, and the strength breaks down after two days, as an unaccelerated mixing would do under similar circumstances. Considering that the short cure is an over-cure, mixing A possesses very good ageing properties.

Mixing B appears to be very outstanding in ageing qualities. In the case of the short cure the load slowly rises to a maximum which is reached in 5 days, and then gradually diminishes. The long cure reaches its maximum in two days. Both heats must, therefore, have been under-cures, although the longer heat is practically a correct cure. In neither case is there much increase in toughness, nor does either heat show signs of breaking up after 10 days in the oven. The strength of the longer heat is still at 1·41 kg. per sq. mm. after 10 days, which is quite outstanding.

TABLE VII.

Mixing A.	Cure ½ hr. at 135° C.			Cure 1½ hr. at 135° C.		
Age in days	Load. kg./mm².	Final length. %	Toughness 700% load. kg./mm².	Load. kg./mm²	Final length. %	Toughness 700% load. kg./mm²
0 ..	1·63	370	0·94 ..	1·76	373	0·96
2 ..	1·70	384	0·91 ..	0·52	573	0·81
4 ..	1·56	384	0·73 ..	0·69	539	0·99
6 ..	1·39	396	0·71 ..	0·25	542	—
8 ..	1·34	717	0·79 ..	0·18	374	—
10 ..	0·40	579	0·74 ..	0·18	340	—
Mixing B.	Cure ½ hr. at 135° C.			Cure 10 hr. at 135° C.		
0 ..	1·56	345	0·89 ..	1·68	367	0·95
2 ..	1·63	356	0·90 ..	1·70	370	0·94
4 ..	1·65	366	0·87 ..	1·61	365	0·86
6 ..	1·49	379	0·82 ..	1·44	354	0·85
8 ..	1·37	341	0·81 ..	1·45	350	0·84
10 ..	1·34	361	0·81 ..	1·41	356	0·82

From this it is evident that D.P.G. mixings show good ageing qualities when subjected to artificial ageing. On the whole, it is probable that mixings containing a small quantity of sulphur age better than those containing a large quantity, but there appears to be not the least danger in using a large quantity. The smallness of the increase in toughness as D.P.G. mixings age may prove a valuable property.

Besides the possibility of the use of an accelerator spoiling the ageing properties of rubber, another contingency which has to be guarded against is the possibility of the accelerator being sufficiently active to cause premature vulcanisation while mixing operations are being carried out, or during subsequent calendering or extruding of the mixing. This phenomenon is one which does not lend itself very

readily to strictly accurate investigation. However, an attempt has been made to deal with the problem in the following way. The mixing chosen contained rubber 100, zinc oxide 5, sulphur 7½, and D.P.G. 1%, and was one of the fastest curing D.P.G. mixings obtainable. Small portions of the mixing were put into a mould similar to those used for the oil-bath method of heating (Comm. Netherlands Govt. Inst., 1917, 139). After clamping up, this mould was placed in a water-bath which could be kept at any desired temperature up to boiling point, and allowed to remain for 5 hours. Samples were heated at 70°, 78°, 88°, 93°, and 97° C. After heating, each sample was carefully examined for signs of curing, a good test being to note the behaviour on passing through a hot mill. The samples heated at 70° and 78° showed no signs of vulcanisation. That heated at 88° was just set. In the case of the 93° and 97° samples, there was no doubt that some vulcanisation had taken place. The critical temperature of this accelerator is, therefore, somewhere about 88° C. That is to say, below that temperature there is either no vulcanisation, or the process is so slow as to escape detection. There is, however, another factor to be considered in connexion with premature vulcanisation, that is the rapidity with which the acceleration increases as the temperature rises above the critical value. The actual investigation of this at low temperatures would be laborious if not impossible, but from the known acceleration at 135° C. it appears that the acceleration will not increase sufficiently rapidly round about 100° to render premature vulcanisation a danger. This becomes more evident when the actual temperature reached on a mixing mill is considered. The temperature of several batches was taken immediately after removal from the mixing mill. As these batches were from 50 to 100 lb. in weight, and were in the form of compact rolls, the temperature of the centre of a roll will be a good indication of the temperature reached on a mixing mill. This was observed for a variety of technical mixings and found to vary from 81° to 85°, which is below the critical temperature for D.P.G. There should, therefore, be little danger of premature vulcanisation in the case of D.P.G. mixings, particularly when it is remembered they will only be at that temperature for a short time.

In considering the milling and mixing of accelerated mixings, another interesting point arises. It is well known that a number of organic accelerators have a marked depolymerising effect on rubber, and therefore they may be used to reduce the time of grinding necessary before solid materials can be incorporated. D.P.G. possesses this property in no inconsiderable degree, as will be seen by the following experiment.

A batch of rubber was ground for 20 minutes and 1% D.P.G. added during the last two or three minutes. Another similar batch was ground for the same length of time, but the 1% D.P.G. was added at the start. When solution viscosities of the two rubbers had been determined by means of the Ostwald viscosimeter it was found that the first batch gave a viscosity number approximately twice that of the second batch. This indicates that by the addition of D.P.G. to rubber before grinding or at the start of grinding, less time will be required to reduce the rubber to a certain degree of plasticity than if no accelerator had been present.

Summary.

The conclusions reached in this paper may be summarised as follows :—

(1) Diphenylguanidine possesses accelerating powers of the same order as *p*-nitrosodimethylaniline.

(2) Diphenylguanidine improves the strength and toughness of mixings and imparts flat-curing properties.

(3) The optimum quantities of diphenylguanidine and sulphur are ½ to 1% of the former, and 5 to 7% of the latter.

(4) This accelerator gives similar results with mixings compounded with zinc oxide and light magnesium carbonate. It is more satisfactory, however, with large quantities of magnesia than with zinc oxide.

(5) Brown and white substitutes appear to have a retarding effect, and such mixings do not give good results.

(6) Diphenylguanidine mixings possess excellent ageing qualities when subjected to artificial ageing tests, particularly if the sulphur content is low.

(7) There appears to be little danger of premature vulcanisation when this substance is present in mixings.

(8) Diphenylguanidine possesses the property of softening rubber.

In conclusion, the author has to acknowledge his indebtedness to the management of the North British Rubber Co., in whose laboratories the above investigation was carried out, for permission to publish this paper.

Castle Mills, Edinburgh.

W. Speight and Sons, Ltd., Printers, Paton Yard, London, E.C. 4

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Hartjens varied the conditions of manufacture in order to trace the origin of these spots or patches and came to the conclusion that they could be connected with the use of sulphite and bisulphite of soda, or a combination of both. Small amounts of these chemicals seldom produce spots, but larger proportions may produce very dark and distinct spots.

It is, therefore, possible that these dark spots are in some way connected with mould growth and also with the use of sulphite and bisulphite in sheet manufacture. There are insufficient data to explain what the connection may be. Possibly the dark parts retain more moisture than the light and are therefore more prone to develop mould. In any case, the observations call for an investigation of the effect of sulphite and bisulphite on the liability of smoked sheet to go mouldy.

Sodium sulphite is used in only very small quantities to keep the latex fluid, but bisulphite is sometimes used in larger quantities to keep the sheet light in color, owing to the marked objection to so-called "oversmoked" sheet. If found that the use of bisulphite tends to cause mould it would probably be better to risk the sheet being dark in color.

It is known that bisulphite hinders the drying of crêpe rubber, that is to say, rubber so treated tends to retain moisture, and what is true of crêpe is probably true of sheet. Sheet which tends to rubber vulcanized in comparison with current samples of the same rubber showed only such small variations as would be found with fresh consignments.

It is evident from the foregoing that deterioration need not take place when ordinary pale crêpe or smoked sheet rubber is stored for long periods under suitable conditions.

Fewer data are available as regards the lower grades, but it is probable that these will keep satisfactorily if properly cleaned and dried. But rubber which contains an appreciable proportion of organic impurity and is exposed to conditions under which putrefaction sets in, will rapidly deteriorate.

"XLO" ACCELERATOR

"XLO" is the trade designation of a recently perfected vulcanization accelerator from which excellent results have been obtained. It is specially recommended for automobile tire stocks, inner tubes and high-class mechanical goods. It is magnesiated di-phenylguanidine in the constant proportions of one-third of the former to two-thirds of the latter. From one-quarter to three-quarters of one per cent of the rubber content of a mixing are the recommended proportions of this accelerator to be used in practical work.

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zum Stelle des Rohres über dem Platinquarz als farbloser, amorpher Beschlag absetzte.

Als ich nach beendigter Analyse den unverändert aussehenden Platinquarz prüfte, zeigte es sich, dass er seine Fähigkeit, im Gasstrome weiter zu glühen[1]), vollständig eingebüsst hatte (trotzdem stimmte die Analyse mit der mittels Bleichromat ausgeführten fast genau überein).

Eine Probe stark »activen« Platinquarzes wurde beim Zusammenglühen mit jenem zur Analyse verwendeten Quarz ebenfalls wirkungslos.

Die Asche im Schiffchen wog 0.0200 g (Zinndioxyd) bei 0.1514 g Substanz. Es fehlen somit ca. 0.01 g, die sichtlich zum allergrössten Theil am Glas abgesetzt waren. Es kann sich nach alledem wohl kaum um ein mechanisches Umhüllen des Platins durch das Zinnoxyd handeln[2])

Die »Giftwirkung« des Arsens für Contactmassen ist bekannt[3]). Es ist vielleicht für den einen oder anderen der HHrn. Fachgenossen von Interesse, dass das Zinn eine ähnliche Wirkung ausüben kann.

München, Chem. Laborat. von H. Weil.

83. G. Pellizzari und C. Cantoni: Ueber Diamido-guanidin.

(Eingegangen am 24. December 1904.)

R. Stollé und K. Hofmann theilen in einem der letzten Hefte dieser Berichte[4]) mit, dass sie salzsaures Diamido-guanidin durch Einwirkung von Chlorcyan auf Hydrazin in ätherischer Lösung erhalten haben. Es liegt uns nun daran, festzustellen, dass wir bereits die Einwirkung von Chlor- und Brom-Cyan (1 Mol.) auf Hydrazin (2 Mol.) in wässriger Lösung studirt und dabei das entsprechende Salz des Diamidoguanidins bezw. aus diesem das Pikrat, Chlorplatinat und Benzylidenderivat erhalten haben. Bei Einwirkung von überschüssigem Bromcyan gewannen wir ausserdem das Salz einer cyclischen Verbindung, die wir Guanazin oder *p*-Diimido-hexahydrotetrazin genannt haben.

Das Manuscript der Arbeit haben wir an die Redaction der Gazz. chim. ital. gesandt, die den Empfang derselben unter dem Datum

[1]) loc. cit. S. 11. [2]) Diese Berichte 34, 4080 [1901].
[3]) Diese Berichte 34, 4080 [1901].
[4]) Diese Berichte 37, 4524—4525 [1904].

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31. August 1904 bestätigt, wie man auf dem Umschlag des am 5. October 1904 herausgekommenen Heftes (Gazz. chim. ital. 34, II, Heft 3) liest. Ein ausführliches Referat über unsere Arbeit ist in den Rendiconti della Società Chimica di Roma über die Sitzung vom 23. October (II. Jahrgang, Heft 16, S. 162) erschienen.

Wenn auch die HHrn. Stoll- und Hofmann unsere Arbeit nicht kennen konnten, bitten wir sie doch, unsere Priorität anzuerkennen und uns zu gestatten, das Studium der erhaltenen Producte fortzusetzen.

Genua, Allgem. chem. Univ.-Inst.

54. A. Kliegl: Ueber Phenyl-fluoren

(Mittheilung aus dem chem. Laborat. der Akad. der Wissensch. zu München.)

(Eingegangen am 21. December 1904.)

Von den bei Beginn der vorliegenden, auf Veranlassung von Hrn. Geheimrath v. Baeyer unternommenen Arbeit (1902) bekannten Darstellungsmethoden des Kohlenwasserstoffes erschien, nachdem Triphenylchlormethan durch Gomberg's Synthese[1]) so leicht zugänglich geworden war, am zweckmässigsten die Destillation äquimolekularer Mengen von Triphenylchlormethan und Triphenylcarbinol[2]). Indess ergaben die angestellten Versuche so geringe Ausbeuten, dass die Gewinnung grösserer Mengen Materials auf diesem Wege unmöglich war[3]). Dagegen wurde in der Destillation von Triphenylcarbinol mit krystallisirter Phosphorsäure eine handliche Methode gefunden, die Phenylfluoren mit guter Ausbeute liefert.

Im Verlauf der Untersuchung wurde ferner zur Darstellung des Kohlenwasserstoffes auch von der Reducirbarkeit des Carbinols Gebrauch gemacht. Das Carbinol selbst kann synthetisch erhalten werden durch Condensation von Fluorenon und Brombenzol mittels Magnesium[4]).

[1]) Diese Berichte 33, 3144 u. f. (1900).

[2]) E. u. O. Fischer, Ann. d. Chem. 194, 259 (1878).

[3]) Eine Notiz Gomberg's (diese Berichte 37, 3545 (1904)) veranlasst mich, zu muthmaassen, dass das von E. u. O. Fischer verwendete Triphenylchlormethan — dargestellt aus Triphenylcarbinol und Phosphorpentachlorid — durch Phosphoroxychlorid verunreinigt war. Daher ihre bessere Ausbeute.

[4]) Die vorliegende Arbeit erschien in München im Sommer 1903 als Dissertationsschrift. Eine Mittheilung darüber in diesen Berichten hat sich leider bis jetzt verzögert. Inzwischen haben Ullmann und v. Wurstemberger (diese Berichte 37, 73 u. f. (1904)) die Darstellung von Phenylfluorenol

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PLAINTIFF'S EXHIBIT No. 28

Berichte der Deutschen Chemischen Gesellschaft, 1905, volume 38, p. 283-284

Translation

53. G. Pellizzari and C. Cantoni. On Diamido-Guanidin

(Received December 24, 1904)

R. Stolle and K. Hofmann report in one of the last numbers of this Berichte[1]) that they have obtained the hydrochloric acid compound of diamido-guanidine by action of chlorcyan on hydrazine. It is guanidin by action of cholrcyan on hydrazine. It is now incumbent on us to report that we have already studied the action of chlor- and bromcyan (1 mol.) on hydrazine (2 mols.) in aqueous solution and thereby obtained the corresponding salt of diamidoguanidin, and from this the picrate, chlorplatinate, and benzylidene derivatives. By the action of bromcyan in excess we also obtained the salt of a cyclic compound, which we have named guanazine or p-diimido-hexahydrotetrazine.

We sent the manuscript of this work to the editor of the Gazz. Chim. Ital., who noted its receipt as of August 31, 1904, as may be seen from the cover of the issue which appeared on Oct. 5, 1904 (Gazz. Chim. Ital., 34, II, Heft 3). An extensive review of our work appeared in the Rendiconti della Societa Chimica di Roma concerning the meeting of Oct. 23 (vol. 2, No. 16, p. 162).

If Messrs. Stolle and Hofmann were unaware of our work we would ask them to acknowledge our priority and allow us to continue the study of the products obtained.

Genua, General Chem. Univ.-Inst.

(Here follows Plaintiff's Exhibit No. 29, marked side folio pages 90, 91, 92, 93, and 94)

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[1] This Berichte, 1904, v. 37, p. 4524-4525.

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The Institution of Rubber Industry.

DR. LOTHAR E. WEBER on ACCELERATORS.

American Expert's Interesting Survey of Accelerator Usage.

The last meeting of the session of the Institution of Rubber Industry was held at the hall of the Royal Society of Arts, John Street, Adelphi, London, W.C., on Friday, the 12th inst., when Dr. Lothar E. Weber delivered a lecture on the practical uses of accelerators in the U.S.A. Mr. D. Zorn occupied the chair.

The chairman, introducing the lecturer, said that he felt it to be a particular pleasure to occupy the chair that night—which he did unexpectedly—because they had to welcome Dr. Lothar E. Weber, who was the son of Dr. C. O. Weber, whose name was a household word to those who understood the technical side of the history of the industry. One of the things which appealed most to him was the fact that Dr. Weber came from the United States. As they had heard him say before, he felt it to be a particularly desirable thing that all the interests of the Rubber Industry in the United States and in this country should draw together and knit up. In the past there had been too much of an idea that there must be a necessary clash of interests between the American manufacturing industry and the planting industry which was almost entirely British. That notion was gradually passing away—and it was high time, too—because the conditions at present surrounding the industry made it absolutely necessary to get rid of all prejudices and to draw together in every way. He understood that Dr. Weber had spent seventeen years of his life in England, and he (the speaker) felt that they could regard him as a link between the two countries. He did not pretend to know much about the technical side of the Industry—his connection with it was from the financial standpoint—but he knew enough to know that Dr. Weber was one of the most famous chemists in the whole Industry, and that he was known throughout rubber circles in America for his work in that direction. He thought they would feel privileged in listening to him that evening, and on behalf of the Institution extended to him an exceedingly hearty welcome. Before sitting down, he referred to what he called general topics. As some of them were aware, a very important public meeting was held the week before at Winchester House under the auspices of the Rubber Shareholders' Association, and at that meeting a definite policy was put forward which would affect the whole of the Rubber Industry. The speech in which that policy was defined would be printed in pamphlet form during the next few days. He had heard that evening with a great deal of pleasure that that policy had been considered by the committee of that Institution, who had decided to support it in every respect. That was very encouraging because any effort to bring about a conference was apt to be met with a very heavy shower of cold water, and the fact that the Institution had adopted that policy was, he thought, a thing which might be helpful in the efforts he was making towards more harmonious working.

Dr. L. E. Weber then spoke as follows:—

Ladies and Gentlemen, during the last five or six years very marked development has taken place in the United States in the application of accelerators. Prior to, let us say, 1916, the number of concerns using organic accelerators in regular factory operation was small. In the year following, 1916 and 1917, more and more concerns began to interest themselves in the utilisation of these materials, so that to-day scarcely a concern of standing in the industry is known that does not use accelerators as part of their regular factory operation. To the casual student of accelerators, probably, the first thing that impresses him is the large number of substances which appear in the literature on the subject, and are characterised as being accelerators, and as being available for factory procedure. Anyone wishing to utilise an accelerator or accelerators would probably be somewhat bewildered, but as a matter of fact there are relatively few accelerators which have found practical application, because other properties are necessary than the mere fact that the substance in question will accelerate the vulcanizing process.

Qualities of a Good Accelerator; Low Critical Temperature; No Discolouring Effect on Goods or Toxic Effect on Operators; and Low Price.

I think at the outset it might be desirable if I referred briefly to the qualities which a substance must possess in order that it may be qualified and regarded as an accelerator from the practical standpoint. In the first place, there is a question of what may be called the critical temperature of the accelerator; that is to say, the temperature at which the substance begins to exert its accelerating action. This temperature must not be too low—by too low I mean in the vicinity of 220 degrees F.—as otherwise premature vulcanization will take place during the mixing and calendering operations.

Importance of Low Critical Temperature in Large Scale Mixing.

This applies particularly to the large scale mixing operation as it is carried out in the United States to-day, and probably here. It is not at all unusual for a factory in the States to employ eighty-four inch mixing mills with a batch of 400 lb. Such a batch naturally gets very warm. The calendering operation also is done on a large scale basis. Calenders frequently run as fast as thirty-five or forty yards a minute—frictioning calenders in frictioning canvas—so that the heat generated in the milling and calendering operations is more than sufficient to start a premature vulcanization unless the critical temperature of the accelerator is relatively high. This property of premature vulcanization is usually known as scorching. You are familiar with it, and a scorched batch is absolutely useless. One might think the more active the accelerator the lower its critical temperature, but such is not the case. Many of the most active accelerators have relatively high critical temperatures, and this of course makes them very desirable. On the other hand, a substance like thiocarbanilide, a relatively weak accelerator, has a low critical temperature, and in the course of years thiocarbanilide has come to be regarded with disfavour in the United States on account of its scorching tendency.

Another property which an accelerator must have is that it must not discolour the vulcanized stock. Such

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discoloration may be immediate, that is, immediately after the stock is vulcanized, or such discoloration may be subsequent, that is to say, it may develop in the course of time. Aniline formaldehyde, a very desirable accelerator in certain respects, is somewhat of an offender in this respect. The articles are white immediately after being vulcanized, but in the course of time—a week or two weeks—are apt to develop a disagreeable yellowish colour. Paranitrosodimethylaniline is looked on with disfavour for the same reason; it tends to discolour the stock.

Toxic Effect of Various Accelerators.

A third property which the accelerator must have, and a most important one from the point of view of factory operations, is freedom from toxicity. A great deal of trouble has been caused in the United States from accelerator poisoning. Factories have had to shut down because their men got into a condition where they were simply not able to work. The accelerators behave in various ways from the standpoint of their toxicity. Aniline oil, as you know, produces what may be called a constitutional toxicity, affecting not only local portions of the skin, but causing a breakdown of the blood cells, resulting in very disagreeable poisoning. The use of aniline oil to-day in the States is small. There are a few concerns that still use it, and those that do use it are able to do so only because they provide for very thorough and rigid ventilation. The stocks in which they use the aniline oil are apt to be stocks that do not require much milling; that is to say, stocks in which the amount of aniline oil that is vaporised is very small. Various methods have been suggested for counteracting or overcoming the aniline oil poisoning. Giving the afflicted workmen milk is of some value, and I believe the use of acetic acid in small quantities has been fairly successful. But aniline oil is not a very desirable accelerator, on account of its poisonous action. Other forms of poisoning are pronounced dermatitis, that is to say, skin irritation. Hexamethylene tetramine is a real offender in this respect. "Hexa" has been used for a great many years, but a great deal of trouble has been caused by it.

The Element of Freakishness.

The extent of the trouble and its seriousness varies very much with the factory. One factory may have relatively good luck; another may not be able to use it, even the men who wrap the tyres in the wrapping rooms being affected. I know one case where the "hexa" had to be thrown out of the factory on account of the irritation which it caused, and for some months after "hexa" had been entirely eliminated the rash still appeared. It was finally traced to the liners. The liners that were used for several months after the abolition of the "hexa" were those which had been utilized with it, and the small amount in the liners was enough to cause skin irritation to the workmen susceptible to it. Some of the other accelerators are not poisonous; they do not produce the effects that aniline oil produces, neither do they produce dermatitis, but they do evolve irritating gases, which the workmen find very disagreeable, and rightly so. An accelerator such as aniline formaldehyde is very desirable in all respects, but aniline formaldehyde gives off formaldehyde, and the workmen find the fumes most disagreeable.

Then a fourth factor in determining the desirability of an accelerator is its price—of course by price being meant the price per active unit. An accelerator costing 5s. a lb., which is three times as active as one costing 2s. 6d. a lb. is the more desirable product to use. You have, first of all the question of scorching; you have in second place the question of toxicity; you have in third place the question of discoloration; and fourthly question of price; all to be considered in selecting accelerator. I think if you will apply these four conditions to the formidable list which you will find in various publications, you will be narrowed down to relatively few substances that meet all these four requirements.

Use in Moulded Goods.

The application of accelerators varies considerably with the goods in which they are used, or more strictly varies with the procedure or the process by which goods are made. It has been found that accelerators work to best advantage in moulded goods; in fact, think I shall be safe in saying that ninety-five per cent of the moulded goods produced in America to-day contain accelerators. I think that would be a conservative statement to make. I was going to put it at ninety-eight, but I think we can call it ninety-five and be fairly conservative. It has been found that in steam-cured goods accelerators should be used with caution. They are used widely to-day in the States in steam-cured goods—certain accelerators—but one is liable to encounter trouble. It is much easier to over-step the mark in steam-cured goods than in the case of press-cured goods. Of course the same applies to steam-cured and press-cured without the accelerator, but I think it is much more marked when the accelerator is present.

Water Solubility of Accelerators as Affecting Steam Cure.

Certain of the accelerators are soluble in water. "Hexa" is the best example; urea, a very desirable accelerator in several respects, is another example. This water solubility is liable to cause considerable trouble, the trouble being that great variation in the cure is experienced, due to removal of the "hexa" by the steam. Naturally the controlling factor is the extent of thoroughness of the wrapping. On a laboratory scale the operation can be readily controlled, but only with difficulty on a factory basis. For this reason variation in the finished product occurs unless very thorough preventative measures are adopted. The use of accelerators in steam-cured goods, to my mind, should be attempted only after one is thoroughly conversant with the use of accelerators in moulded articles.

Reasons for Non-employment of accelerators in Dry Heat Cure.

In the dry heat cure accelerators have found very little application. In fact I do not think accelerators are used at all in dry heat cure, because the presence of litharge is a disturbing factor—most of the accelerators being poisoned by litharge. Relatively few per cent.—six or eight per cent.—of litharge in a compound makes the action felt quite markedly in killing the activity of the accelerator, or probably, more exactly, in forming lead salts instead of zinc salts. The lead salts, for some reason do not seem to be as active as the zinc, but I do not want to get into any discussion on the theoretical action of accelerators. The fact of the matter is that in dry heat accelerators are not used at all.

I would like now to take up the accelerators which are used most frequently, and state briefly the proportion in which they enter into compounds, and the question of

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ence of the mineral oxide, usually zinc, which in some has to be present and in other cases need not be.

ine Oil Little Used To-Day.

he accelerator which may be called the parent of the erators used to-day is aniline oil. Aniline oil was quite extensively in the United States at one time. is a very desirable accelerator viewed purely from celerating process. Not only does the aniline an accelerating action, but it exerts also a pro- ed solvent action on the rubber, which probably in explains why aniline oil has so little tendency to h. It is used to the extent of about 2 per cent. d on the rubber present. If the compound contains er cent. of rubber the customary amount of aniline ld is 1 per cent. I do not want to give you an ression that that is an absolute rule, it is not; many nufacturers would use as high as 3 or 4 per cent. d on the rubber. As to the amount in the compound it goes into the presses, that is another matter, as niline being quite volatile goes off into the air, and nless the manufacturer who insists on using that unt of aniline oil is doing little else than evaporating bulk of it into the atmosphere. But I think would be perfectly safe in using 2 per cent. pure gum compound, just rubber and sulphur, it would dvisable to go lower, say 1 per cent. It is desirable ave zinc oxide, but not imperative. Aniline ac- ates the process equally well in the presence or nce of zinc oxide. The use of aniline oil to-day is ll; the number of concerns using it has decreased, ause too much trouble was experienced with poisoning.

arbanilide—The Most Widely Used Accelerator

he accelerator which probably followed aniline oil rically is thiocarbanilide; it is the accelerator used t widely; the largest number of firms use thiocar- ide. One must differentiate quite clearly between the ber of concerns using an accelerator, and the total unt of accelerator used in the industry; because there five concerns in the United States—who in their pro- ion probably outweigh the combined production of the r concerns, and of course if one of these very large erns uses a particular accelerator, it naturally in- es the proportion of the total amount of that ac- rator consumed. Thiocarbanilide is probably accelerator which is used by the largest number oncerns, and that notwithstanding its very disagree- tendency to scorching. This tendency is not alto- er an unmitigated evil, because, if the calendering mixing operations are not on too large a scale—if re on a more modest, every-day scale—by carefully olling the conditions of temperature, in fact keeping onditions of temperature down to the really desirable , scorching does not take place, and any evidence corching can be regarded by the works manager as ence of carelessness on the part of the factory rator. To be sure in the warm weather this considera- does not apply. Neither does it apply in the case ery quick curing compounds or in the case of com- nds containing a high percentage of mineral fillers, characterised as "dry" on the mixing mill. In e of its shortcomings thiocarbanilide still holds a high place among accelerators in the United States. e again the customary amount is about 2 per cent. the rubber present. Zinc oxide should be used, as accelerator is much more active in the presence of oxide.

he figure of 2 per cent. which I gave is by no means exact; in very quick-curing compounds 3 or even 4 per cent. is used, though from the standpoint of good ageing, in my opinion, the amount should not be much in excess of 2 per cent.

The Second Accelerator in Popularity (Hexamethylene Tetramine).

An accelerator closely following thiocarbanilide in popularity is hexamethylene tetramine. A great deal of "hexa" poisoning has taken place, but were it not for this poisoning tendency "hexa" would be an extremely desirable accelerator. Its price per active unit is quite low. It can be obtained in large quantities and in a state of reasonable purity. In the case of "hexa" about one to 1½ per cent. is a desirable limit; I would not wish to say that 2 per cent. would cause difficulty, but it is desirable to employ "hexa" in smaller quantities. I think it will be found in the case of "hexa" that increasing the amount of the accelerator does not necessarily proportionately increase the speed of the cure. Of course it is very difficult talk in general terms on the activity of any accelerator, because other ingredients in the compound exert such a powerful influence. This consideration is just the same in the case of the inorganic accelerators. Supposing you ask a man what is the relative amount of, let us say, lime, in comparison with six ounces of sulphur; if you eliminate six ounces of sulphur but of your compound, how much lime should you put in to get the identical result? Of course that question cannot be answered, and just so, or more so, do similar conditions obtain in the case of organic accelerators. But talking generally, I would say that 1½ per cent. of hexamethylene tetramine represents the desirable upper limit. In the case of "hexa" it is desirable to have zinc oxide present —not entirely necessary, but preferable.

Aniline Formaldehyde; A Desirable Accelerator.

Aniline formaldehyde is an accelerator which is increasing in popularity. It is relatively cheap. It can be produced in large quantities, is active, and is relatively free from showing scorching and any toxic action other than slight irritation owing to the fumes evolved; but if the workman is at all careful he need not suffer from the irritating fumes of aniline formaldehyde. Aniline formaldehyde, in my opinion, is a very desirable accelerator. Here again the amount to be used is in the vicinity of 1½ to 2 per cent. based on the rubber present, and zinc oxide is desirable.

Aldehyde Ammonia and the Guanidine Derivatives.

Aldehyde ammonia at one time held some popularity, but it has the objection of being very active and tending to produce scorching. Aldehyde ammonia is much more active than aniline formaldehyde, "hexa" or thiocarbanilide. I would say that 1 per cent. based on the rubber present would represent the upper desirable limit for aldehyde ammonia.

During the last two years guanidine derivatives have come into favour, notably the di-phenyl-guanidine and the tri-phenyl-guanidine. The di-phenyl-guanidine is considerably the more active of the two, but both the "di" and the "tri" are very desirable accelerators. They don't scorch, don't discolour, are non-poisonous, and are obtainable at a reasonably attractive price per active unit. I think that di-phenyl-guanidine and tri-phenyl-guanidine are probably a little more expensive than thiocarbanilide, but not very much so, that is, based on the active unit. These materials are coming into increasing favour in the United States, and in my opinion represent very desirable accelerators. The di-phenyl-guanidine

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should be used in amounts, I would say, not exceeding three-quarters of 1 per cent. based on the rubber present. It is a very active substance. One per cent. might be all right, but I think three-quarters would be a little safer. The "tri" is not quite so active, and I think that 1¼ or 1½ per cent. is safe.

Sodium and Lead Oleate.

There are one or two accelerators that have found application in the past, but are now little used, namely, sodium and lead oleate. They are desirable because they are cheap, and certainly in the case of sodium oleate non-poisonous. Whether the lead oleate is non-poisonous is open to doubt. When lead oleate is used it can be made simply by adding a lead acid to a litharge compound; sodium oleate is used as such. Oleic acid, I think, can be classified as the original organic accelerator.

The accelerating action of oleic acid was accidentally discovered in my father's laboratory in Boston as early as 1904, in the course of some work on castor oil. It was found that rancid castor oil gave a very much better vulcanized product than castor oil which was not rancid. This, of course, led to the theory that the free acid was doing the accelerating, and the addition of oleic acid proved this theory correct. From then onwards in the States oleic acid and the closely related stearic acid were both used in very large quantities for increasing the speed of cure of weak African rubbers, which fifteen or twenty years ago were available in large quantities. Stearic acid is still used in the States, though not as an accelerator, but in place of palm oil for softening stocks on the calender.

Markedly Poisonous Accelerators.

Paranitrosodimethylaniline has some friends in the United States, but it is open to the objection of being markedly poisonous, and the number of concerns using this accelerator is small. Paraphenylenediamine at one time had a few friends, but to my mind the use of this substance in the Rubber Industry is an outrage. Owing to its frightfully poisonous nature it has no place in the rubber factory.

The Advantages of Using Accelerators.

Now a few words with regard to the advantages of accelerators. First and foremost, of course, is the matter of decreased cure. Accelerators have been used chiefly in moulded goods, and of course the length of the cure is of enormous importance in this line of manufacture, because the factory output is determined purely and simply by the length of cure. So it is fortunate that accelerators are of most advantage in this particular class of work, where added equipment is expensive and sometimes cannot be installed. It is doubtless the savings effected in this respect which are largely responsible for the rapid advance in the use of accelerators in the United States. Take tyres: the output of a tyre factory is partially limited by its milling and calendering capacity, but chiefly by its moulding and curing capacity. If you cut the length of cure in half you come very near to increasing your output by one-third, so the chief advantage of accelerators is that of decrease of cure, and in that manner enabling you to turn out a larger output. The decrease in overhead and fixed charges is obvious.

A second advantage of accelerators is that they decrease the tendency to over-cure. This statement will be questioned probably. What I mean is that in the presence of an accelerator, notably "hexa" and the guanidines, an increase in the conditions of cure which would ordinarily result in an over-cure does not bring about a state of over-vulcanization. The presence of an accelerator, when used in its proper amounts, makes the compound less susceptible to over-vulcanization.

In the third place, and I think this statement will not be doubted, a properly vulcanized accelerator compound ages better than a properly vulcanized compound without an accelerator. By that I do not mean to say that an accelerated compound is fool-proof; but a compound containing an accelerator, if vulcanized correctly; that is to say, if precautions are taken to make sure that the compound is not over-vulcanized, ages better than a similar correctly vulcanized compound without the accelerator.

Precautions to Secure Ageing Qualities.

In closing I would like to offer, if I may, one or two suggestions as to the manner in which a manufacturer could proceed if he was desirous of using an accelerator but was somewhat afraid that his product would not act satisfactorily, or that he would run into serious difficulties of some kind or another. The great danger in using an accelerator is over-cure. An accelerated compound which may appear properly vulcanized need not necessarily be correctly vulcanized unless one is assured that a decrease in cure will result in an under-vulcanized compound. In other words, if one adds an accelerator one should start an experiment by working upwards from a condition of under-cure. An under-cure is very readily recognized of all; the difficulty lies in recognising the over-cure. Having got this state of under-cure, the cure should then be raised until what is ordinarily regarded as a good cure is obtained. By following the reaction in this manner the danger of over-cure is small. On the other hand, if an article is cured, and an examination shows it to be unsatisfactory merely from the standpoint of tensile, elongation and permanent set, one cannot be assured that a decreased cure will not result in just the same physical conditions, and one should take special precautions to preclude the possibility of over-vulcanization

The Accelerated Ageing Test.

I believe that last year Dr. Geer spoke to you about the accelerated ageing test which he has been using for eleven or twelve years. I do not know how popular the accelerated ageing test is in England, but I would heartily commend it to the attention of every manufacturer. The accelerated ageing test is not fool-proof, considerable judgment has to be used in interpreting the results obtained. One should always age, simultaneously with the sample under examination, a stock of essentially similar composition, the ageing qualities of which are accurately known. If operated in this manner, and if precautions are taken to ensure a reasonable flow of new air into the ageing oven, results of great value are obtained.

Personal Experience.

I have had actual experience with the accelerated ageing test for somewhat over ten years, and I frankly say that so dependent have I become upon this ageing test that I am very reluctant to pass any opinion on a cure without first subjecting the sample to the action of an elevated temperature. Dr. Geer uses 70 deg. C., I happened to start with 65 deg. C., and for no reason at all other than that it gives good results have stuck to it. It does not make much difference, I think, whether you use 65 or 70. The important thing is to age, simultaneously with the sample under examination, another sample of similar composition and of known ageing quality. This is very readily possible in the case of experimental samples that come

erator, it being merely necessary to age, simultaneously with the accelerated sample, a sample of the stock free from the accelerator, and compare results. If a manufacturer proceeds in this manner, I have no hesitation in saying that he can develop the use of accelerators successfully in a reasonably short period of time. I would certainly suggest that natural ageing tests — let us say, from four to six months, should always be employed. But in the course of six months a manufacturer should be in a position to tell with safety and surety that an accelerated compound will age, and will act satisfactorily. (Applause.)

THE DISCUSSION.

The chairman regretted that his knowledge of technical matters was so small that it was impossible for him to put questions. One point that struck him as a layman, however, was that the address appeared to have touched on exceedingly practical lines. He would set the ball rolling by asking when accelerators first came into use.

Dr. Weber said that it was his understanding that accelerators were first used on a commercial scale by the Diamond Rubber Company in 1906, and shortly afterwards thiocarbanilide was introduced either by the Diamond Company or the Goodrich Company, probably about 1908. Up to 1915 the number of concerns using accelerators was small, but from then on progress had been rapid.

Mr. Noah (International Rubber Co.) asked what accelerator could be used in a mixing that contained antimony sulphide.

Dr. Weber said it would be perfectly safe to use hexamethylene tetramine or triphenyl guanidine. It was stated by some manufacturers of antimony that accelerators should not be used in addition with the latter pigment, but the fault lay with the antimony and not with the accelerator.

Mr. Noah inquired whether triphenyl guanidine was active in the absence of zinc oxide.

Dr. Weber said he could not definitely answer that question. He thought it probable that the accelerator would be active in the absence of zinc oxide, but the activity would be increased when zinc oxide was added.

Dr. H. P. Stevens said that the lecture had been very interesting. He was pleased to see that Dr. Weber had not been able to get down to actual manufacturing procedure. In the past they had not heard much about that; they all seemed to fight shy of coming down to tintacks. With regard to scorching, he understood that was more likely to take place on large machines. Was that really so, or was it possible to have efficient cooling of the rollers? In this country many manufacturers showed a preference for smaller machines because they could be kept under control. He also asked whether Dr. Weber had had any experience with so-called super-accelerators. The difficulty which they found with them was that vulcanization set in spontaneously, causing the batch to be wasted, but these so-called super-accelerators had most remarkable properties, and it was possible to use 1 or 2 per cent. of sulphur and to get vulcanization at a very low temperature. Provided they met with no insuperable difficulty, they should come into wide use. Had the lecturer any experience of them?

Dr. Weber, referring to the question of scorching, said that theoretically the larger mills should be equally as efficient as the smaller ones, but in actual practice this was not found to be the case, and the danger of scorching on the large mill was much greater. In the United States they had a disagreeable temperature problem to contend with, and in the summer they were liable to have a midday temperature of 85 to 95 for weeks at a stretch. This was quite usual in July to have an average midday temperature of 89. In summer the question of keeping the mills cool was much greater, and the manufacturer who met with the most serious trouble was the one who employed large mills. With regard to the use of sulphur, it was well-known that the presence of an accelerator resulted in a decreased vulcanization co-efficient. Whereas the accepted co-efficient is 2.8 to 3, in the presence of organic accelerator co-efficients of less than 1 appear to be quite satisfactory. The trade tendency towards non-blooming compounds was diminishing in the States. Manufacturers found that non-blooming compounds were undesirable from a manufacturing standpoint and the tendency was for blooming compounds wherever possible. Dr. Weber then emphasised the danger of over-curing, when accelerators were present. In the early days, he said, over-curing was not recognised, and he wished he had the income on the capital that had been lost on that account. With regard to super-accelerators, he thought they were at present of purely laboratory interest. They certainly had big possibilities, but not with the present methods of manufacture.

Mr. S. J. Peachey, referring to aniline oil, said that his experience was that it was not used because of its acceleration properties, and he would like to hear whether it was a fact that it was used in the United States because of its softening qualities only.

Dr. Weber said that aniline oil was an accelerator of the vulcanizing process, although there was a danger of losing a proportion of the aniline oil added to the compound owing to its volatility and especially in highly compounded stocks, which require considerable mixing.

Mr. Peachey referred to the difference between aniline oil and paranitiosodimethylaniline and asked what were the relative activities of the two.

Dr. Weber said that while the question was difficult to answer accurately, he thought that the paranitiosodimethylaniline was at least four times as strong as aniline oil.

In answer to Mr. Fordyce Jones, the lecturer said that the whole philosophy of accelerators was directed towards increasing the output of the plant. Regarding the acceleration of reclaimed rubber, it was found that this material was not very susceptible to the action of accelerators. In the case of compounds containing reclaimed rubber, the acceleration observed was doubtless due to the action of the accelerator on the crude rubber, which was nearly always present to some extent, rather than on the reclaimed rubber. Regarding the present consumption of reclaimed rubber in the United States, while it was of course true that the tonnage consumption had decreased during the depression period, the ratio of ultilisation of crude and reclaimed rubber had decreased only slightly. Accurate statistics on that point were available from the published figures of the Rubber Association of America. Those statistics showed that in normal times for every pound of crude rubber used in the industry 0.7 lb. of reclaimed rubber was consumed. Owing to the fact that oil substitutes found very little application in compounding in the States, the rubber scrap available to the reclaimer was very well adapted for reclaiming and a thoroughly high grade reclaimed rubber was obtained. The American compounder had come to regard reclaimed rubber, not as a filler, but as fulfilling a definite function in the compound, and results were obtained by the use of reclaimed rubber which could not be obtained in any other way.

The chairman said that Dr. Weber had cheered him up somewhat by mentioning that there was a shortage of some sort in connection with rubber. (Laughter.) But unfortunately one swallow did not make a summer. He wondered whether Dr. Weber could give him the name of an accelerator which would accelerate the consumption of surplus rubber—that was the accelerator he wanted.

Mr. Fordyce Jones, proposing a vote of thanks to the lecturer, said it was very difficult for Britishers to express their appreciation in words, and he thought that he was only voicing the thoughts of the meeting by suggesting that Dr. Weber should take their appreciation without words. That Institution stood for the very thing that Dr. Weber was one of the first to fulfil. The lecturer had not only done a great thing for their Institution, but a great thing for the British Rubber Industry. America consumed 75 per cent. of the rubber consumption of the world, and they, as Britishers, wanted to feel that they were not competitors, but that they had the same ideals and wished to pull in the same path. While that was a very small meeting, he wished Dr. Weber to realise that he had addressed the whole British Rubber Industry, which was eagerly waiting to hear what he had said through the medium of the Trade press.

Mr. Rogers, seconding, said that he had listened to the paper with very great interest indeed. At the last Rubber Exhibition he had heard the paper by Dr. Geer on Ageing, and he was pleased to find that Dr. Weber followed on the same lines on the question of temperature.

The vote was carried by acclamation, and on the proposition of Dr. Stevens a similar vote was accorded Mr. Zorn for presiding.

The chairman, in reply, said that his impression of that meeting was that it was the most interesting of any spent at the Institution of Rubber Industry. 94

PLAINTIFF'S EXHIBIT No. 30

Application of Morris L. Weiss. Ser. No. 490,746. Filed Aug. 8, 1921. For Improvement in Accelerators for the Vulcanization of Rubber

Specification

To all whom it may concern:

Be It Known That I, Morris L. Weiss, a citizen of the United States and resident of the Borough of Brooklyn, County of Kings, State of New York, have invented certain new and useful improvements in—

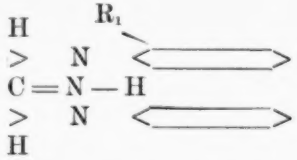
Accelerators for the Vulcanization of Rubber of which the following is a full, clear, concise and exact description:

The object of my invention is to produce a substance which will accelerate the vulcanization of rubber and similar substances through its catalytic action on the rubber and on the vulcanizing agents when used therewith, so that the rubber is cured or vulcanized more quickly and with a smaller amount of vulcanizing agents than heretofore have generally been used.

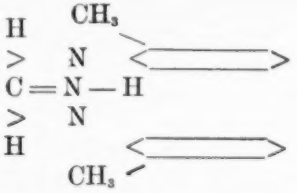
During my work relating to the production of guanidines, particularly diphenylguanidine, I discovered that certain substituted guanidines obtained from primary aromatic amines containing hydrocarbon residues comprising those termed hydrocarbon or alkyl groups in the ortho position, and produced from substituted aromatic thioureas containing alkyl groups in the ortho position relative to the nitrogen of the thiourea, have the beneficial and valuable action, when used as accelerators, of enabling rubber to be cured or vulcanized in a relatively shorter time than heretofore has been necessary in the usual vulcanizing operations under steam pressures and temperatures commonly used.

Furthermore, I have found that the accelerated action in the vulcanization of rubber is produced by comparatively small quantities of the accelerating compound, so that there is no undesirable loading or adulteration of the rubber compound, which is maintained in its original color and texture when completely vulcanized. In fact, the use of my improved accelerator improves the final quality and texture

of the rubber and also increases its durability, and it is less liable to air vulcanization and blooming. The class of chemical substances in which the improved accelerator constituting my invention is found may be represented by the following formula:



In this formula R_1 may represent any hydrocarbon or alkyl radical such as CH_3. This, of course, may be either in one phenyl group as indicated in the above formula, or in both phenyl groups, such as symmetrical di-ortho-tolyl guanidine represented by the formula—



The groups of aromatic amines referred to, as well as the thiourea derived therefrom, comprises the xqlidins, amino-cymenes, cumidins and napththyl amines.

The process of carrying out my invention which I at present deem preferable may be illustrated by the following example:

The rubber is compounded in the following proportions:

50		parts by weight of raw rubber
45	75	" of zinc oxide
3	5	" of sulphur
	.75	" of di-ortho-tolyl guanidine.

These are mixed together in any suitable way, such as by milling, and vulcanized or cured in the usual moulds or otherwise under a steam pressure of substantially 40 lbs. per square inch. This vulcanizing temperature should be continued until the compound is suitably vulcanized, which

requires from 10 to 20 minutes, depending on the amount or size of the articles being vulcanized.

I have found, however, that with lower steam pressure and consequent reduction of temperature vulcanization will also proceed to the desired point but requires a slightly greater period of time. Thus, it is obvious that the temperature may be reduced, if desired, with the consequent advantage of eliminating the possibility of the rubber being burned or overcured.

Having thus described this example of the invention and the method of using the same, I do not wish to be understood as being limited to the exact proportions, ingredients, temperatures, etc., etc., indicated, for various changes may be made without departing from the essential features of my invention, as set forth in the accompanying claims.

What I claim and desire to protect by Letters Patent is:

1. The process of treating rubber or similar materials which comprises combining with the rubber compound an aryl substituted guanidine having an alkyl group in the ortho position.

2. The process of treating rubber or similar materials which comprises combining with the rubber compound an ortho-tolyl guanidine.

3. The process of treating rubber or similar materials which comprises combining with the rubber compound di-ortho-tolyl guanidine.

4. The process of treating rubber or similar materials which comprises combining with the rubber compound a substituted guanidine accelerator having an alkyl group in ortho position and derived from a primary aromatic amine.

5. The process of treating rubber or similar materials which comprises combining with the rubber compound a substituted guanidine accelerator having a methyl group in ortho position and derived from a primary aromatic amine.

6. The process of treating rubber or similar materials which comprises combining with the rubber compound a substituted guanidine accelerator derived from ortho-toluidin.

7. The process of treating rubber or similar materials which comprises combining with the rubber compound a vulcanizing agent and an aryl substituted guanidine accelerator having an alkyl group in ortho position.

8. The process of treating rubber or similar materials which comprises combining with the rubber compound a vulcanizing agent and an ortha-tolyl guanidine.

9. The process of treating rubber or similar materials which comprises combining with the rubber compound a vulcanizing agent and di-ortho-tolyl guanidine.

10. A vulcanized compound of rubber or similar material combined with a vulcanizing agent and an oryl substituted guanidine accelerator having an alkyl group in ortho position.

11. A vulcanized compound of rubber or similar material combined with a vulcanizing agent and an orthotolyl guanidine.

12. A vulcanized compound of rubber or similar material combined with a vulcanizing agent and diortho-tolyl guanidine.

13. A vulcanized compound of rubber or similar material combined with a vulcanizing agent and a substituted guanidine accelerator having an alkyl group in ortho position and derived from a primary aromatic amine.

14. A vulcanized compound of rubber or similar material combined with a vulcanizing agent and a substituted guanidine accelerator having a methyl group in ortho position and derived from a primary aromatic amine.

15. A vulcanized compound of rubber or similar material combined with a vulcanizing agent and a substituted guanidine accelerator derived from ortho-toluidin.

(Signed) Morris L. Weiss.

(Here follows Plaintiff's Exhibit No. 31, marked side folio page 100)

PLAINTIFF'S EXHIBIT NO. 21

100

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DEFENDANT'S EXHIBIT "A"

United States District Court, Southern District of New York

In Equity

DOVAN CHEMICAL CORPORATION, Plaintiff,

vs.

NATIONAL ANILINE & CHEMICAL COMPANY, INC., Defendant

On Patent No. 1,411,231, to M. L. Weiss

Affidavit of M. L. Weiss on Motion for Preliminary Injunction

STATE OF NEW YORK,
County of New York, ss:

Morris L. Weiss, being duly sworn, deposes and says as follows:

I am the Morris L. Weiss who has heretofore made an affidavit in this cause dated May 26, 1922. In addition to my former affidavit, I depose and say as follows:

When I entered the employ of the Republic Rubber Company at Youngstown, Ohio, on October 18, 1917, I was assigned to analytical work relating to the manufacture of rubber goods and among such analyses I was asked to analyze and test certain organic substances known as accelerators for use in vulcanization of rubber compounds. During my work on such substances during the spring of 1918, it occurred to me to try dis-ubstituted guanidines, particularly diphenylguanidine as an accelerator for rubber vulcanization. This occurred to me without any previous suggestion, direction, or information from anyone whomsoever as I had never previously known or heard of the use of diphenylguanidine as an accelerator in rubber vulcanization. I had, however, at that time, made some tests on triphenylguanidine as an accelerator for rubber, this substance having been prepared by me in the course of my work to ascertain its action in vulcanization as I had been informed that it had been used to some extent by the Republic

Rubber Company prior to my being employed there. In June, 1918, I took my vacation and went to New York and visited the New York Public Library at 42nd Street and Fifth Avenue, to look up various questions relating to accelerators, such as their poisonous nature and other questions. This was at the request of Mr. Monroe H. Daniels prior to my leaving on my vacation. Having had diphenylguanidine previously in mind I particularly noted reference to the same when looking for publications relating to triphenylguanidine, paraphenylenediamine, etc. As a result of this examination at the New York Public Library, I found very little literature on diphenylguanidine but found sufficient data to enable me to prepare a small quantity of diphenylguanidine, which I did during the month of September 1918. The quantity produced at that time was not sufficient to permit a test in a rubber compound. During my conversations with Mr. Daniels in the month of September 1918, I mentioned to him my tests of triphenylguanidine and advised him that I desired to also try diphenylguanidine to ascertain whether it would be a good accelerator, and told him that I was at that time trying to produce a sufficient quantity to test it in a rubber compound in the laboratory. At that time I did not have sufficient data to produce any considerable quantity of diphenylguanidine, and therefore, in January 1919, I visited the library of the Carnegie Institute at Pittsburgh, Pennsylvania, and went through the literature on this subject. As a result of this investigation I found descriptions of various processes for making diphenylguanidine by laboratory methods and upon my return to Youngstown, Ohio, about the middle of the same month, January 1919, I prepared sufficient diphenylguanidine and tested it soon thereafter in a rubber compound. During the month of February I continued tests on diphenylguanidine by mixing it with various rubber compounds, the results of which are shown in the book now in possession of the Republic Rubber Company at Youngstown, Ohio, known as the Chemical Laboratory X Book. The entries in this book were made in my own handwriting as concerns my personal experiments with and test of diphenylguanidine. Having found that the diphenylguanidine seemed to act as a good accelerator, I immediately started to develop a process by which it could be produced

cheaply in commercial quantities. This work continued until the end of the year 1919 in addition to my regular duties as head of the analytical department of the chemical laboratory, tests on diphenylguanidine as an accelerator also being conducted from time to time during that period. Early in the year 1920, I completed the process for manufacturing diphenylguanidine in commercial quantities and at a reasonably cheap price and on or about the 2nd day of March 1920, I submitted a report to the Republic Rubber Company, stating the results of my experiments and the results of my work in producing a process of manufacturing the accelerator. An exact copy of the original report is attached hereto, marked "Weiss Exhibit A" and is dated March 2, 1920.

During the latter part of February, I was advised that my services would not be required after the 15th of March, and, therefore during the first week in March I went to Akron, Ohio, and visited the factory of the Firestone Tire and Rubber Company with a view to obtaining a position with that company. At the factory of the Firestone Tire and Rubber Company, I met Mr. N. P. Shepard, who was the research chemist, and gave him the original copy of my report disclosing the process for the manufacture of diphenylguanidine similar to that in Weiss Exhibit A. Said Shepard expressed interest in the accelerator and process of making the same and asked a number of questions concerning my experience, but after leaving the factory, I was advised by him that there was no opportunity at the factory of the Firestone Tire and Rubber Company. During my conversation with Mr. Shepard, he stated to me that he would refer the matter to a Mr. Young, the chief chemist. A few days later said report was returned to me at Youngstown, by the Firestone Tire and Rubber Company by mail without any accompanying letter but a letter was later received stating there was no vacancy. I left the employ of the Republic Rubber Company, on or about the 15th day of March 1920 and came to New York to look for employment in that city. As stated in the bill of complaint and in my prior affidavit executed May 26, 1922. I then visited the office of the defendant, 21 Burling Slip and the office of Mr. Henry S. Doty and Mr. Van Lear Woodward and other chemical concerns in New York City. I have read the affi-

davits of Messrs. Henry S. Doty and Van Lear Woodward made in this case and aver that the statements made therein concerning the starting of the business relating to the manufacture of diphenylguanidine, its development and present condition, are true to the best of my knowledge, information, and belief. I would say, however, that during the fire which occurred at the Brooklyn factory in September, 1921, many of my notes and records were destroyed, said notes and records including those that I had made while with the Republic Rubber Company of Youngstown, Ohio.

I have read all of the eight answering affidavits submitted by the defendant in this cause. Regarding the affidavits of Corl H. Eaton and Carl H. Zieme both executed June 3, 1922, I would say that the statements made therein regarding the alleged early disclosure of diphenylguanidine as an accelerator by said Eaton to said Zieme are untrue to the best of my knowledge and belief and that the statement that said Eaton suggested to me that diphenylguanidine would be a better accelerator than triphenylguanidine because of its higher nitrogen content is wholly untrue and without foundation.

Said Eaton was employed by the Republic Rubber Company only as an analytical chemist on routine work during the latter part of the year 1918 and the first part of the year 1919 as it was the policy of the Republic Rubber Company to give newly employed chemists general analytical work only for the first year or so of their employment in order that their knowledge and capabilities could be determined before special or research or any other work was entrusted to them. Consequently, it was not until after the middle of the year 1919 that I may have had any conversation with said Eaton concerning accelerators for rubber vulcanization, particularly in view of the fact that I considered him not sufficiently familiar or experienced in the chemistry relating to rubber and organic synthesis to understand or do work in organic accelerators, as he had been previously employed as a chemist for the Youngstown Sheet & Tube Company. Up to the latter part of the year 1919, said Eaton was fully occupied with routine analytical work as were the three or four other analytical

chemists employed under me at that time. Furthermore all work carried on by the assistant chemists in my department was embodied in written reports which were sent to me and which I had copied in typewriting and submitted to the respective assistants for their signatures. These reports were always dated and one copy was sent by me to the chief chemist, at that time Mr. Monroe H. Daniels, and a carbon copy retained in my files in the analytical laboratory. I am, therefore, sure that said Eaton did not make any suggestion to me as he alleged, for if he had done so I should have immediately told him of my prior work on diphenylguanidine and would have advised him of my intention to continue the same.

The statement made by said Eaton that he actually used diphenylguanidine as a rubber accelerator during the month of January 1919 and at various times thereafter is also to the best of my knowledge and belief untrue. None of the analytical chemists were permitted to do compounding work in the chemical laboratory or elsewhere and all of the compounding relating to accelerators or other new ingredients of compounds were conducted by myself or under my direction.

Regarding Eaton's reference to his notebook I would say that he had no desk used solely by himself there being only one desk used by the three or four other assistants in the analytical laborartory, in which desk the notebooks provided by my department for recording data were kept. These notebooks were of the kind usually used by stenographers and large numbers of these books were thrown into the various drawers of this desk and practically discarded after having served their purpose. All valuable data which it was desired to preserve was copied from these books and embodied in the reports above referred to. As to the implication made by said Eaton that his notebook containing data relating to diphenylguanidine or any other records relating thereto were taken from his desk, I would say that there is absolutely no foundation therefor, particularly as it is obvious that the destruction or the taking of such notebooks from the desk would have made no difference because all valuable data relating thereto would have been recorded in the reports above mentioned.

I have read the affidavit of Monroe H. Daniels, executed June 10, 1922 and aver that the statements made therein regarding the relations between Carl H. Zieme and said Eaton are true to the best of my knowledge and belief and therefore consider it contrary to fact that said Eaton disclosed to said Zieme that he was working on the production of diphenylguanidine or that he proposed to use the same as a rubber accelerator. From my intimate knowledge of the work of the chemical laboratory I am positive that said Eaton never did any work on the production of diphenylguanidine during my connection with the Republic Rubber Company.

It is possible that said Zieme and said Eaton may have had some conversations regarding diphenylguanidine as an accelerator during the month of December 1919 or one year later than the alleged time. This seems particularly to be the fact in view of the absence of any written records of the Republic Rubber Company indicating such work and such work could not have been continued at all during the year 1919 without having come to the knowledge of Monroe H. Daniels or myself. Furthermore in the latter part of the year 1919 I personally told said Zieme that I had produced diphenylguanidine as an accelerator for rubber compounds, that I was working on a process for manufacturing the same in sufficient quantities for use in the factory and that I intended to use it in hose compounds he being superintendent of the hose departments. At that time said Zieme did not mention to me that anyone else connected with the Republic Rubber Company had been working with diphenylguanidine as an accelerator.

I have read the paragraph of the affidavit of Mr. Monroe H. Daniels dated June 10, 1922, concerning said Daniels' conversation with said Eaton after the meeting of the American Chemical Society in September 1919 and believe that said paragraph states the true fact and that the next succeeding paragraph relating to said Daniels' conversation with me states the fact in that regard because I distinctly remember that said Daniels told me that the paper read by said Kratz at said meeting confirmed our experience with diphenylguanidine as an accelerator and that we should continue our work on that substance and develop a commercial process if possible.

I have examined the photographic copies of the pages of the laboratory X-book No-. 2006, 2034 and 2042 attached to said Daniels' affidavit as "Daniels' Exhibit B" and recognize the same as being correct copies of the said pages of said book kept by me and recorded in my own handwriting. I also recognize the photostat copies of said pages and the additional pages 2010 and 2059, 2060, 2064, 2065, and 2066 as being copies of pages from said laboratory X-book, which copies are attached to the affidavit of said Corl H. Eaton the handwriting thereon being my own with the exception of the letters "C_6H_5 COOH", the figures "9-15-17", the word "magnesia" and the figures in the second ruled column. The references on these pages to diphenylguanidine, diffendo and other accelerators indicate compounds suggested by me and actually tested by vulcanizing the same which tests were made on or about the dates indicated by the figures at the bottom of the ruled columns. The earliest date mentioning diphenylguanidine as having been used is "2-10-19" on sheet No. 2034. The next earliest date is "2-21-19" on sheet No. 2036 but the latter date has an arrow below it pointing to "compare with X 2005 H". The latter sheet X 2005 having column H thereon, I understand from the affidavit of said Eaton was missing from the book and therefore could not be copied. I am at a loss to understand why this page should have been extracted from this book as I am positive that the same was in the book at the time I left the Republic Rubber Company and believe that the same was taken out by someone adversely disposed toward my interests. I certainly did not remove this or any other page from that book.

Said Eaton states that on page 2034 the date "9-10-19" was apparently changed to "2-10-19." If any change were made as regards these figures the change was from a "1" to a "2" instead of from a "9" to a "2", January being the next preceding month to February. If any such change were made, it was made on February 10, 1919 and not subsequently thereto as seems to be implied by the statement of the said Eaton. Regarding the last paragraph of said Eaton affidavit, I would state that the same is incorrect and does not state the fact. Work was carried on by me to develop a process of producing diphenylguanidine in com-

mercial quantities at various times during the entire year of 1919 and a large number of experiments were made to test the various methods described in the literature and to develop other methods which might be more efficient. Toward the end of the year 1919 a new method was developed and tested on a semi-commercial scale and this is substantially the process disclosed in my application Serial No. 482,143 filed July 2, 1921, for Process of Making Diphenylguanidine as an Accelerator for Rubber Vulcanization. A certified copy of said application is submitted herewith marked "Weiss Exhibit B". This process is substantially the same as that set forth in "Weiss Exhibit A" of March 2, 1920 and which indicates the very extensive work made necessary to develop the process, it being obvious that such work could not have been started and completed between November 1919 and the latter part of February 1920 in addition to my other duties made necessary by virtue of my position as the head of the analytical laboratory.

Regarding the affidavit of Norman A. Shepard dated June 5, 1922 and submitted by the defendant it is true that I did make application for employment at the Firestone Tire & Rubber Company, Akron, Ohio, about March 3, 1920 and I talked with said Shepard at that time. I did not make any statement or assertion to have originated the use of diphenylguanidine as an accelerator because I considered that the main difficulty in its use was that of finding a process to produce the material in substantial practical quantities and I emphasized that fact rather than the fact of my having originated its use. My reference to the article by Kratz was simply by way of corroboration of my work as to the activity of diphenylguanidine as an accelerator, as shown by my notes made on the application blank, copy of which is attached to said Shepard affidavit. Furthermore I was not confident that any part of a group of organic compounds, some of which had been used as accelerators for rubber, could be patented as such because I had been so informed prior to my leaving the Republic Rubber Company when discussing the subject with a party adversely disposed toward my interest. This impression was corrected by patent counsel for the Dovan Chemical Corporation when considering the applications

for the Process of Making Diphenylguanidine above referred to as "Weiss Exhibit B". I had always considered that I was the originator of diphenylguanidine as an accelerator for rubber and had never heard of any consideration whatever of it by others until my talk with Monroe H. Daniels after his return from Philadelphia in September 1919.

I have read the affidavit of John Young executed June 8, 1922 and would state that any recollection which said Young may have had relative to my reference to the Kratz paper is apparently based only upon an examination of the written application in which I mentioned the paper for the same reasons and without in any way giving credit to said Kratz for having discovered the advantages of diphenylguanidine as a rubber accelerator. I had no conversation whatever with Mr. Young.

I have also read the affidavit of Alfred L. Loebenberg executed June 8, 1922 and state that the reference made to Dr. Kratz during my conversation with said Loebenberg was for the same reasons above mentioned in connection with the Shepard affidavit and I in no way conveyed to him any statement that I did not consider myself the originator of diphenylguanidine as an accelerator.

Regarding the letter under date of April 13, 1920, mentioned in the Loebenberg affidavit I would say that I do not recollect ever having received such a letter but I did return to the office of the National Aniline & Chemical Company about a week after my first visit and was simply requested to fill out another application blank without seeing Mr. Loebenberg or anyone whom I had before known. I filled out the second application but never thereafter received any reply to the same.

Morris L. Weiss.

Sworn to and subscribed before me this 12th day of June 1922. Walter S. Jones, Notary Public, New York Co. (Seal.)

8:21

Dept Ex 22c

NATIONAL ANILINE & CHEMICAL CO., INC. 1/3/23 Ex 14

Ex 13

10/17/23 HC

APPLICATION FOR EMPLOYMENT 6-14-23

DATE 10 Oct 2-1918

NAME M. J. Lewis — POSITION DESIRED Research Chemist — APPLICATION NUMBER 4629

DATE AVAILABLE Immediately — LOCATION DESIRED Jersey City — SALARY DESIRED $2400 a year

TEMPORARY OR PERMANENT Permanent — IF CONTRACT REQUIRED Renewable — MINIMUM ACCEPTABLE $2400 a year

PRESENT ADDRESS 614 W 138th St N.Y.C. — PHONE 3334 Audubon

PERMANENT ADDRESS — AGE AT DATE OF APPLICATION 28

PREVIOUS EMPLOYMENT

DATE	POSITIONS AND DUTIES	COMPANY NAME AND BUSINESS	ADDRESS
1913-1918	Asst Research Chemist	Herman Frasch Laboratory	50th St & 10th Ave City
1918-1922	Research Chemist	Republic Rubber Co	Youngstown, Ohio

SCHOOLS ATTENDED	DATES FROM	DATES TO	COURSES AND STUDIES	DEGREE AND DATE
Rogers Institute	1908	1913	Chemical	Diploma 1913
Polytechnic Institute	1913	1916	College Chemical	B.S. in Chem 1916

PERSONAL REFERENCES	ADDRESS	OCCUPATION	NATURE AND EXTENT OF ACQUAINTANCE
Dr. S. Grunwald	Harriman Research Lab. Harriman, N.Y.	Research Chemist	Has employed me since graduation
H. L. Fisher	Harriman Research Lab. Harriman, N.Y.	Research Chemist	Associate at Harriman
Wm. M. Daniels	2109 Elm St Youngstown, O.	Asst Chemist	Employed me as Asst Chemist at Youngstown, O.

PUBLICATIONS, INVENTIONS, PROFESSIONAL ACTIVITIES "The Fate of Diphenylcarbazone in Titrations" S. Grunwald & M. L. Weiss Journ. of Biological Chem July 1917

LANGUAGES SPOKEN OTHER THAN ENGLISH German and French

MILITARY AFFILIATIONS AND ACTIVITIES (PAST AND PRESENT) None

NATIONALITY American — DATE OF FIRST PAPERS — DATE OF FINAL PAPERS

MARRIED OR SINGLE married — DEPENDENTS

PHYSICAL CONDITION Good

PHYSICAL DISABILITIES, ACCIDENTS, FAILURES None

HEIGHT 5 ft 9 inch — WEIGHT 170 lbs — ENDURANCE good — VITALITY good

114

Defendant's Exhibit B (Page 1)

8:23'

Work at Republic Tire + Rubber Co -
Development + manufacture + application
of accelerators - Amline, TCA,
diphenylguanidine triphenylguanidine
aldehyde &c — (also Nitroso Duals)

1 - Amline = .8 Thio
1 - Diphenylguanidine = 4 Thio
1 - " - 4 Triphenyl - (Ethanol)
1 - Diphenylguanidine = 1½ Thiocarbanilide

Ac Knafy

Defendant's Exhibit B (Page 2)

Ex. No. 2
U. S. Dist. Court,
S. D. of N. Y. 74-13

Dfts Ex C
10/19/45

FIRESTONE TIRE & RUBBER COMPANY
AKRON, OHIO

APPLICATION

No.

All information given in this Application will be treated as confidential matter by the company. By carefully and freely answering EACH of the questions on this application you will assist us in determining whether any personal trait or fact disqualifies you for service. It is desired that no space be left blank. If any question does not apply to you, so state. Please write in the applicant's own handwriting.

Name of applicant M L Meiss Date Mch 7 1916

Present Address 1196 Donaldson Ave Youngstown Ohio Phone No

Home Address New York City

Have you previously filed application with us? No Physical defects, if any None

The company requires applicants to pass a physical examination by its examining physician before they are accepted as employees.

Month	Day	Year	AGE Years	AGE Months	PLACE OF BIRTH	CITY	STATE
June	8th	1887	33	2			Russia

HEIGHT	WEIGHT	LINEAGE	Are you a Citizen of the United States?	If Not a Citizen, State When
5 ft 2 inches	118 lbs	English, Irish, French, Hebrew, German, Etc. 6	Yes	Mch 15th 1914

	FATHER	MOTHER	PLACE OF BIRTH	FATHER	MOTHER
	Hebrew	Hebrew		Russia	Russia

	Single	Married	Divorced	Number of Children	Number of Other Dependents	Relationship of Dependents
				None	None	

RELATIONSHIP	NAME	ADDRESS
Brother	A M Meiss	1727 Park Pl Brooklyn N Y

LIFE	HEALTH	ACCIDENT	PHOTOGRAPH	Whenever possible attach to this Photograph of yourself. If you do not, please enclose one in passage
$1000				

Of whom, among those connected with the Company, are you acquainted?

Mr. Heller, Compounding chemist, Mechanical goods Dept

EDUCATION

SCHOOL OR COLLEGE	ATTENDED From Year	ATTENDED To Year	COURSE OF STUDY	PROFICIENCY
Cooper Institute N Y C	1905	1912	Technical Chemistry	Good
Pratt Institute Brooklyn N Y	1913	1916	College course	

GIVE ANY ADDITIONAL INFORMATION REGARDING EDUCATION

I have also taken a course in physiological chemistry at Columbia University New York City

Defendant's Exhibit C (Page 1) 116

BUSINESS EXPERIENCE REFERENCES

EMPLOYER (Give full Name of Company or Firm)	CITY AND STATE	KIND OF BUSINESS	TIME EMPLOYED From Mo. Yr. To Mo. Yr.	POSITION YOU HELD	Salary or Wages	WHY DID YOU LEAVE?	CITY NUMBER OF BODY AND BOY UNDER WHOM YOU WORKED	HIS PRESENT STREET, CITY AND STATE ADDRESS	HIS PRESENT BUSINESS OR POSITION
1 Harriman Research Lab & J.C.	New York	Research Laboratory	Jan 1917 Feb 1917	Research Chemist	154	Suffered pay	Dr. J. Brannan	Roosevelt Hosp 59th St & 9th Ave N.Y.C.	Regional Chemist
2 Butterworth Judson Co	Newark N.J.	Manufacturing Chemists	Feb 1917	Research Chemist	154	Left Hamilton	Dr. A. L. Hamilton, M.D. Dr. H.H. Daniels	123 Rubber Co Youngstown Ohio	Asst. Chemist
3 Republic Rubber Co	Youngstown Ohio	Rubber Goods	Feb 1917	Asst. Research Chemist	$2.00			Elm St Youngstown Ohio	Asst. Chemist
4									
5									
6									
7									
Present Employer									

May we refer to your present employer? _____

BUSINESS REFERENCES OTHER THAN FORMER EMPLOYERS

NAME	ADDRESS	BUSINESS OR OFFICIAL POSITION	STATE PERSONAL RELATION
Dr. K. Sverge Falk	Harriman Research Lab & J.C.	Research Chemist	—
Dr. E.M. Fowler	" " " "	" "	"
Dr. L.J. Curtman	College of the City of New York	Asst. Professor of Chem.	—
Jno. A. Brannan	The Bryant Press & J.C.	Owner	Brother-in-law

State fully the lines of work in which you are proficient, your qualifications therein and your preference:

At the Harriman Research Laboratory I have been working in Biochemical research. I have done all the analytical work and a good deal of organic problems connected with the research problems. My name appears as collaborator on a paper published in the Journal of Biological Chem. for July 1917.

At the Butterworth Judson Co I worked on the commercial synthesis purification and methods of analysis of accelerator ingredients.

At the Republic Rubber Co I have developed a process for the manufacture of Carbamate, which is being worked successfully now. I have also developed a process for the manufacture of Thiocarbanilide which is worked successfully now in preference to their old process. By this process a 98% pure product is obtained without recourse to recrystallization. I have lately developed a process for the commercial production of Aldehyde Ammonia. The value of this product as an accelerator has been discussed by Dr. Keaty at the last Philadelphia meeting of the Am. Chem. Soc. and tests made on a basis he has shown that .05% of this product is equivalent to 1.0% of Amiline. This product is not being produced now as all development work has been stopped. However I prepared enough of it on a semi-commercial scale to test it out in the laboratory and plants. The laboratory tests show that one part of the product is equivalent to 4 parts of Thiocarbanilide and 10 parts of Tetramethyl Thiuram. It is a pure crystalline compound more hygroscopic and volatile and more poisonous. The cost of this product will be 3.50 to 4.00 cents a pound less than Thiocarbanilide. I did not get a chance to try it in the factory.

Salary Desired $ 250 per month — Least Salary Considered $ 200

The Space below to be Filled out by a representative of the Company

Recommended for _____ Department

At Salary of $ _____ per _____ Date Employed _____

Interviewed by _____ ; _____ ; Date _____

Interviewed by _____ ; _____ ; Date _____

Remarks: _____

Defendant's Exhibit C (Page 2) 117

Defendant's Exhibit "E."

[Reprinted from the Journal of Industrial and Engineering Chemistry.
Vol. 12, No. 4, page 317. April, 1920.]

The Action of Certain Organic Accelerators in the Vulcanization of Rubber

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By C. D. Kratz, A. H. Flower and Cole Coolidge

[Reprinted from the Journal of Industrial and Engineering Chemistry, Vol. 12, No. 4, page 317, April, 1920.]

THE ACTION OF CERTAIN ORGANIC ACCELERATORS IN THE VULCANIZATION OF RUBBER[1]

By G. D. Kratz, A. H. Flower and Cole Coolidge

RESEARCH LABORATORIES, THE FALLS RUBBER COMPANY, CUYAHOGA FALLS, OHIO

Since the introduction of the use of organic substances to assist in, or to accelerate, the vulcanization of rubber, there has been remarkably little added to the literature upon the subject. Furthermore, what has been written has been confined largely to reviews of a general nature. Although King,[2] Peachey,[3] Twiss,[4] Spence,[5] and others[6] have contributed to this subject, the majority of investigators have remained reticent, despite the fact that the patent files are replete with information.

The present paper records a portion of the results procured in an attempt to obtain further information in regard to the action of certain organic substances in accelerating the vulcanization reaction. Throughout this work we have chosen to employ only substances which have previously been cited by others and whose definite chemical composition permits comparison with homologs or other closely related compounds. The activities of the substances from a practical standpoint were considered of secondary importance. Further, while we most assuredly recognize that the vulcanization reaction is, essentially, a catalytic one, we have chosen to employ the term "accelerator" rather than "catalyst," when referring to the organic substances in question. This distinction is deemed necessary to avoid misunderstanding, and to discriminate between catalysis as it is generally understood and as it must be applied to the vulcanization of rubber. In this regard, it is necessary to take into consideration the fact that a large number of the organic substances used to accelerate the vulcanization of rubber de-

[1] Presented before the Rubber Division at the 8th Meeting of the American Chemical Society, Philadelphia, Pa., September 2 to 6, 1919.

[2] *Met & Chem. Eng.*, 15 (1916), 231; 18 (1918), 246.

[3] *India Rubber J.*, 52 (1916), 603; *J. Soc. Chem. Ind.*, 36 (1917), 321; 36 (1917), 434, 950.

[4] *J. Soc. Chem. Ind.*, 36 (1917), 783.

[5] THIS JOURNAL, 10 (1918), 115.

[6] *Gummi Ztg.*, 29 (1915), 425; 30 (1916), 303; *India Rubber World*, 55 (1917), 190; *Caoutchouc et gutta-percha*, 15 (1918), 9637; *Rubber Age*, 3 (1918), 78.

compose below the temperatures at which vulcanization is ordinarily effected, and that many of them show a tendency to combine with the sulfur under vulcanizing conditions. Again, as most of the rubber mixtures in actual use contain mineral substances, the possibility of a reaction of these substances with the organic accelerators involving the alteration or decomposition of the latter, is far from remote. In fact, even before the general use of synthetic organic substances as accelerators, Esch[1] found it necessary to employ calcium and magnesium oxides with certain albuminous bodies in order to obtain the desired results. Likewise, Peachey[2] has noted a marked increase in the activity of *p*-nitrosodimethylaniline when used in conjunction with magnesia. Litharge was found to diminish the effectiveness of this accelerator.

Although we are confident that the use of organic substances as accelerators was practiced in the factories of this country long before the first patent on the subject was taken out abroad, the predominance of the early patents was undoubtedly German. In fact, the latter people, with their thoroughness and the realization of the possibilities in the subject, attempted to restrict the use of all nitrogenous substances by the use of such generalities as are found in one of Bayer and Company's patents.[3] That few, if any, applications for license to use these patents were made during the war is an indication of our priority in this field.

The first German patents upon accelerators appeared almost coincidentally with certain patents for the preparation of synthetic rubber, when it was found that this substance was abnormally slow in its reaction with sulfur. In this connection, Bayer and Company found that piperidine or its homologs[4] and the piperidine salt of piperidyl-dithiocarbamic acid[5] effected a marked acceleration in the vulcanization of Kondakow's rubber,[6] and, subsequently, they extended their claims to cover natural rubber. Prior to the above Bayer patents, however, a patent was issued to Wo. and Walther Ostwald[7] for the treatment of rubber, gutta-percha, and the like, with pyridine, quinoline, dimethylaniline, etc., in order to prevent

[1] D. R. P. 273,482 (1912).
[2] *J. Soc. Chem. Ind.*, 36 (1917), 424.
[3] D. R. P. 280,198 (1914).
[4] D. R. P. 266,680, 266,618 (1912); 263,387, 265,221 (1913).
[5] D. R. P. 266,619 (1913); U. S. Patent 1,126,469 (1915).
[6] *J. prakt. Chem.*, 64 (1901), 109.
[7] D. R. P. 221,310 (1908).

its becoming hard and fragile. It is most remarkable that in the course of this work the Ostwalds failed to note the action of certain salts of these and other closely related substances in accelerating the vulcanization of the rubber, even though the parent substances themselves possess little, if any, action.

Immediately following the patents for the use of piperidine and its derivatives appeared a variety of specifications covering the use of dimethylamine,[1] aldehyde ammonia, tetra- and hexamethylenediamines, *p*-phenylenediamine, and naphthylenediamines;[2] the formaldehyde condensation products of aniline and its homologs;[3] the guanidines;[4] naphthylamine;[5] and a large number of other amino-compounds, or nitrogenous substances, all of which have been mentioned previously by King, Peachey, Twiss, Spence, or Ditmar, and include such substances as quinoline and its salts, the quaternary ammonium bases, urea and thiourea derivatives, and a host of others. In their patents, Bayer and Company cover the urea and thiourea derivatives of saturated aliphatic amines, both open and closed carbon chains, which are saturated methylene open-carbon chain bases. The term "methylene base" is held to be generic to those bases which are saturated bases as distinguished from unsaturated bases as aniline. Suffice to say, that both aniline and diphenylthiourea were employed in this country long before the appearance of any of the above specifications.[6]

Although not specified in some of the foregoing patents, many of these were drawn upon the assumption that the activities of the various substances depended largely upon their nitrogenous nature and the basicity of the substances in question.

In view of the well-known effect of such inorganic bases as caustic soda or potash upon the vulcanization of rubber, the opinion that the basicity of certain substances is closely connected with their action as accelerators has found quite a few adherents. Among

[1] D. R. P. 269,513; French Patent 464,533.
[2] D. R. P. 280,198 (1914); U. S. Patent 1,149,580 (1915).
[3] British Patent 7,370 (1914).
[4] British Patent 17,760 (1914).
[5] U. S. Patent 1,296,469 (1919).
[6] In this connection it is interesting to note that in this country attention was directed to the use of urea as an accelerator before the appearance of these or any other patents upon urea or the thioureas. This is said to have been the result of observations made upon certain African rubbers, reputed to have been coagulated with human urine, and which were found to vulcanize with more than average rapidity.

these is Twiss,[1] who believes that both the organic and inorganic accelerators, all of basic nature, exert their influence in a similar manner. According to Twiss, the more powerful action of the organic bases is due to their greater solubility in the rubber, a principle which he has applied in preparing very active accelerators by the use of an organic liquid which would be soluble in the rubber and also act as a solvent for alkali. In a subsequent patent[2] he has still further extended this view to include such materials as solutions of sodium and potassium in aniline, the action of which would be difficult indeed to classify if essential differences are held to exist between the action of organic and inorganic accelerators. Peachey,[3] however, in his patent upon *p*-nitrosodimethylaniline, has taken another view, and attributes the activity of this substance, primarily, to the presence of the nitroso group. Subsequently, Peachey[4] has also expressed the opinion that, while the dissociation constant of 1×10^{-5}, referred to in the Bayer patents, does actually form a dividing line between accelerating and non-accelerating bases, there are other classes of accelerators (as *p*-nitrosodimethylaniline) which are not basic, or but slightly so. Further, in order to emphasize not only the effect of certain groups, but also the position of these groups in the molecule, Peachey has cited the nitroso bases as powerful accelerators, and pointed out that the isomeric nitrosamines, in which the nitroso group is not in direct combination with the nucleus are inert.

Likewise, Spence has mentioned that the activity of certain substances which contain groups in the para position are more active than the isomeric substances, in which the groups are in the ortho, or meta position, and has cited the relative activities of *p*-phenetidine and *o*-phenetidine as an example. He has also called attention to the increase effected in the activity of substances as accelerators by the introduction of other groups into the nucleus. As a case in point, he has made reference to the increase in the activity of diphenylthiourea when it is converted into tetramethyldiaminodiphenylthiourea. While there is no doubt that these differences exist as

[1] *J. Soc. Chem. Ind.*, 36 (1917), 782; British Patent 110,059 (1916).
[2] British Patent 124,276 (1919).
[3] British Patent 4,243 (1914).
[4] *J. Soc. Chem. Ind.*, 36 (1917), 950.

expressed by Peachey and Spence, it is to be regretted that no figures were given by either of them by which the relative activities of the various substances might be recorded.

Our own experience, a portion of which is embodied in the experimental part of this paper, in the main confirms the results of Peachey and Spence; and in fact, in many ways, permits of their amplifications. Not only have we found certain groups, and the position of these groups in the primary nucleus, to have a marked effect upon the activity of the substance under investigation, but we have found that if the effect produced by one or more groups is to be considered on a strictly comparable basis, the size (molecular weight) of the parent substance must also be taken into account. On the other hand, we are equally well convinced that with many substances it is possible to place too great stress upon the presence of certain groups and their position in the nucleus. It would appear that the effect produced by the different groups is largely determined by their behavior and ultimate condition as the original substance undergoes decomposition or chemical change, and that the activity of substances not originally basic is due to their conversion into basic substances during vulcanization.

For example, in our preliminary experiments we found that urea was slightly more active than thiourea. Thiourea, in turn, was more active than monophenylthiourea, and the latter more active than diphenylthiourea. The same was true in the case of the guanidines, both monophenylguanidine and diphenylguanidine being found more active than triphenylguanidine, although the conditions of our experiment did not permit of a differentiation between the two substances first mentioned. In the case of the thiourea, the natural inferences would be that the activity of the parent substance depended largely upon the presence of the NH_2 groups, with a consequent diminution in the effect produced as phenyl replaces hydrogen. In the case of the guanidines, the great difference in activities of mono- and diphenylguanidines, when compared with that of triphenylguanidine, may be attributed to the fact that in the latter substance the phenyl group has replaced imido rather than amido hydrogen.

Again, when we made a comparison between a cyclic

monamine and diamine, we found the latter, in accordance with the now general understanding, to be much more active than the former, if the groups are in the para position. On the formation of the anhydro-formaldehyde condensation products of these substances, however, although the activities of each were increased by the substitution of methylene groups for the hydrogen of the amino groups in the original substances, this increase in the case of the monoamine was much less than that produced by the introduction of a second amino group into the original nucleus. Although the two types of compounds are not isomeric, this is in line with Peachey's statement as to the effect produced when groups are introduced into a side-chain rather than the original nucleus.

In our subsequent and more extensive experiments, wherein we employed aniline as a basis of comparison, we found that the replacement of the amino group in aniline by hydroxyl actually decreased the rate of vulcanization to less than that of the control mixture which contained no accelerator. The introduction of a second hydroxyl group in the para position was found to cause a still greater retardation in the rate of reaction. In fact, when allowance was made for the difference in the molecular weights of the two substances, the anti-accelerating effect of hydroquinone was found to be just twice that of phenol. The difference between the effect of one amino group and two amino groups in the para position has already been mentioned, and here again, after having corrected for the molecular weights of the two substances, *p*-phenylenediamine was found to be almost exactly twice as active as aniline. When we employed *p*-amidophenol, however, in order to obtain an amino group and an hydroxyl group in the para position to each other, our results were not strictly in accordance with those of Peachey and Spence, who found that this substance was without action or but mildly active. On the contrary, we found *p*-amidophenol to be more active than aniline. The inference from our results would be that although the effect of the (OH) group is that of a retardant, its position in the nucleus, and its subsequent influence upon the decomposition of the nucleus during vulcanization, are of less importance than the effect produced by the stronger and positive (NH_2) group.

It is not our purpose, however, to attribute the action of certain substances as accelerators entirely

to the inclusion and position of certain groups in the primary nucleus. Rather, as has been said, we have been led to the conclusion that the great majority of organic accelerators owe their activity to their decomposition products, when this decomposition takes place in the presence of sulfur and under vulcanizing conditions. This corresponds very closely with Spence's third class of accelerators, which he believes may be inactive in themselves, but which, at the temperature of vulcanization, either alone or in the presence of other substances, may break down into a substance, or substances, having the properties of powerful catalysts. He has mentioned diphenylthiourea as an example of this type.

In the final experiment recorded in this paper, we have worked along these lines with aniline as a standard and have compared its activity with that of other substances into which it can be converted, or from which it can be derived by decomposition under vulcanizing conditions. The following reaction suffices to explain our method:

$$C_6H_5NH_2 + C_6H_5N{:}C{:}S \rightleftharpoons \begin{matrix} C_6H_5NH \\ C_6H_5NH \end{matrix}\!\!>C : S \quad (1)$$

That such a reaction, from right to left, actually takes place was indicated when we found that a mixture vulcanized with the assistance of a certain definite amount of diphenylthiourea had the same sulfur coefficient as that of a similar mixture, vulcanized under the same conditions, to which had been added aniline and phenyl mustard oil, in accordance with the amounts required by Equation 1. Similar sulfur coefficients also resulted for two mixtures, one of which was vulcanized with the assistance of triphenylguanidine and the other with quantities of diphenylthiourea and aniline, in accordance with Equation 2.

$$\begin{matrix} C_6H_5NH \\ C_6H_5NH \end{matrix}\!\!>C : S + C_6H_5NH_2 \rightleftharpoons \begin{matrix} C_6H_5NH \\ C_6H_5NH \end{matrix}\!\!>C : N.C_6H_5 + H_2S \quad (2)$$

The above reaction, likewise, takes place from right to left. The diphenylthiourea and aniline formed, however, evidently undergo further decomposition

with the formation of two molecules of aniline and one molecule of phenyl mustard oil.

Our interpretation of these results led us to the conclusion that both diphenylthiourea and triphenylguanidine owe their powers of acceleration to their tendency to decompose with the formation of aniline. On the other hand, and in view of our results as a whole and particularly those obtained with urea and thiourea, we certainly do not feel warranted in ascribing to aniline alone those properties which Spence has termed the "active principle." Rather, we are inclined to regard aniline as one of the simpler substances that contains a group which, under vulcanizing conditions and temperatures, functions as a sulfur carrier.

To elaborate upon the action of accelerators beyond this point, however, is hardly warranted from the results obtained. Moreover, further discussion must, necessarily, involve the theory of vulcanization in its entirety, which is not our intention in this communication.

We have shown that under vulcanizing conditions and temperatures, certain accelerators decompose or suffer degradation to simpler substances which are responsible for the acceleration effected. The decomposition of diphenylthiourea to aniline is an example. Such being the case, similar decompositions would appear possible with other substances. This decomposition having been effected, the action of the decomposition or alteration products is most conveniently interpreted on the basis of a change in the valency of the nitrogen in active groups from 3 to 5.

It is not to be understood, however, that we believe aniline as such is, necessarily and quantitatively, formed by the decomposition of diphenylthiourea under vulcanizing conditions. Further, the various complexes which we have postulated for aniline, *p*-phenylenediamine, etc., serve to account only for the relationship noted between the activity of the substance in question and its nitrogen content. Theoretical deductions of a general nature are not at present possible, as results obtained by Erdmann[1] and Ostromyslenskii[2] indicate that the active sulfur may take the form of a polysulfide and may even not be attached to nitrogen. However, for the purpose of interpretation, rather than deduction, and with aniline as an example, under the conditions and tempera-

[1] *Ann.*, **362** (1908), 133.
[2] A. H. King, *Met. & Chem. Eng.*, **15** (1916), 245.

tures at which vulcanization takes place, we postulate the existence of the following complex:

$$C_6H_5 - \overset{\overset{S}{\|}}{N} = H_2$$

As this complex would not be stable, except under the conditions and temperatures at which vulcanization is effected, it would function as a catalytic sulfur carrier, releasing its sulfur in an active form, which would combine with the rubber more readily than the sulfur originally included in the mixture. Its catalytic action would depend upon its ability to maintain an equilibrium between the active and inactive sulfur.

The above is in strict accord with our results for the relative activity of aniline and *p*-phenylenediamine. The hypothetical complex for the latter substance would include 2 pentavalent nitrogen atoms, or active groups, as below:

$$H_2 = \overset{\overset{S}{\|}}{N}.C_6H_4.\overset{\overset{S}{\|}}{N} = H_2$$

Thus, when the effect of molecularly equivalent quantities of aniline and *p*-phenylenediamine are compared, the latter should be just twice as active as the former. This was actually found to be the case. From this it is also possible to explain why Spence found tetramethyldiaminodiphenylthiourea so much more active than diphenylthiourea; the former substance would probably decompose into 2 molecules of dimethyl-*p*-phenylenediamine with just twice the number of active groups found in the latter. Further, we venture to predict that the activity of one molecular part of tetramethyldiaminodiphenylthiourea is exactly equal to that of 2 equimolecular parts of dimethyl-*p*-phenylenediamine,[1] and less than that of 2 equimolecular parts of *p*-phenylenediamine. The difference in the basicities of the last two substances accounts for their relative activities.

[1] It is interesting to note that Eaton, Grantham and Day (Dept. of Agr. Fed. Malay States, *Bulletin* 27 (1918), (319) found dimethyl-*p*-phenylenediamine hydrochloride to exert a marked retarding influence upon the vulcanization of a fast curing rubber. In this case, then, the nitrogen of the amino group is already pentavalent, and could not act as a sulfur carrier; it has already been shown that acid groups act as retardants.

In this connection, it should also be pointed out that although dimethyl-*p*-phenylenediamine is more active than aniline, dimethylaniline is practically inert.

$$\begin{matrix}(CH_3)_2N.C_6H_4.NH \\ | \\ C:S \\ | \\ (CH_3)_2N.C_6H_4.NH\end{matrix} \longrightarrow 2\left\{(CH_3)_2N.C_6H_4.\overset{\overset{S}{\|}}{N} = H_2\right\} \quad (3)$$

The latter observation is made in the light of our results with the ureas and guanidines. While our results with these substances are subject to the same general interpretation as the preceding, we found with them that the replacement of the hydrogen by phenyl in the active groups decreased the activity of the substance in question. It is possible that the substitution of larger groups for the hydrogen attached to the active nitrogen would cause the group to become inactive, due to steric hindrance precluding the formation of pentavalent nitrogen. Peachey's observation of the inactivity of the nitrosamine isomeric with *p*-nitrosodimethylaniline may be subject to this interpretation.

In view of this, our results with the anhydroformaldehyde condensation products of aromatic amines are more difficult to interpret, as the substitution of methylene for hydrogen increased the activity. In this instance, however, there will be two double bonds when nitrogen becomes pentavalent:

$$C_6H_4.\overset{\overset{S}{\|}}{N} = C : H_2$$

A complex of this type would be even more unstable, and more active, than that postulated for aniline.[1]

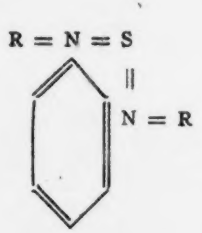
Lastly, in light of the readiness with which sulfur passes from the di- to the tetra- or hexavalent state, it is possible to adapt the former principles to account

[1] In the paper by C. W. Bedford and W. Scott, read immediately after the above, the following explanation was offered for the behavior of this substance. According to the above authors, under vulcanizing conditions and temperature, the following reactions take place:

$$2[C_6H_5N.CH_2] \longrightarrow C_6H_5.N\begin{matrix}CH_2\\ \\ CH_2\end{matrix}>N.C_6H_5 + 4S \longrightarrow$$

$$CH_2 + H_2S + (C_6H_5NH)_2C:S$$

We have already shown that diphenylthiourea probably decomposes into aniline and phenyl mustard oil. Further, we have shown that when compared on equal weights the activities of anhydroformaldehyde aniline and diphenylthiourea are approximately the same. As the molecular weight of diphenylthiourea is over twice that of anhydro-formaldehyde aniline, and as two molecules of the latter and one molecule of the former would each decompose into one molecule of aniline, a comparison with equal weight of the two substances should show anhydro-formaldehyde aniline to be slightly more active than diphenylthiourea. This is in strict accordance with the above reactions and our findings.



(*A*)

(*B*)

for the difference in the relative activities of the *o*- and *p*- products of the same substance. The proximity of two groups in the *o*-position might lead to a complex of type *A*, whereas, if the groups were in the *p*-position, the configuration would be that shown in type *B*.

In this case, then, the *p*- would be twice as active as the *o*-product, a condition with which we are not as yet familiar.

In the foregoing we have not taken into consideration the effect of the accelerators upon the physical properties of the mixtures investigated, and have confined our remarks to interpretations made on the basis of excess sulfur coefficients of vulcanization only. However, in our experiments with mixtures vulcanized with the assistance of aniline, diphenylthiourea and triphenylguanidine, we were able in no instance to recover the original amount of the accelerator in the acetone extract. While this does not permit us to state definitely that a portion of the accelerator or its decomposition products, as well as the sulfur, becomes closely bound to the rubber molecule, it is not impossible that such is the case. We agree with King, that the remarkable improvement imparted to mixtures vulcanized with the assistance of certain organic accelerators indicates that the binding between the "active principle," or active group, of certain of the organic accelerators and the rubber is a close one.

In the course of another investigation shortly to be published, we have shown that fundamental differences exist between vulcanized mixtures of rubber and sulfur, and similar mixtures vulcanized with the assistance of an organic accelerator. This is subject to still further modification if either type of mixture contains a mineral oxide.

EXPERIMENTAL PART

The same general method of procedure was pursued in this work as in that previously reported.

The rubber used was good quality, first latex, pale crepe, and the same lot was employed in all mixtures. All mixtures were made under standard conditions; the average time of each batch on the mill was 17.5 min. The same proportion of rubber and sulfur—92.5 parts rubber, and 7.5 parts sulfur—was employed in each instance, but the amount of accelerator was varied, according to the conditions of the experiment.

All of the accelerators soluble in alcohol were dissolved in the smallest quantity of this liquid and introduced into the rubber in solution. Those not soluble—and this applied to the anhydro-formaldehyde bodies only—were ground to 100 mesh and added to the rubber with the sulfur. After mixing, the mixtures were allowed a recovery period of 24 hrs. before they were vulcanized. Vulcanization was carried on in a platen press of the usual type.

The vulcanized sample for analysis was then sheeted thin on the mill, subjected to 24 hrs. continuous extraction with acetone in the extractor recommended by the Joint Rubber Insulation Committee,[1] dried in air and *in vacuo* at 100° C. to constant weight. The free, or extractable, sulfur found in the acetone extract was estimated by the bromine oxidation method of the Bureau of Standards.[2] The combined sulfur in the extracted rubber was estimated by a method of our own, to be reported upon in the near future.[3] All figures given for per cent sulfur are the average of at least 2 determinations which checked to within 0.1 per cent.

PRELIMINARY EXPERIMENTS — With the exception of aniline, which was purified by distillation and boiled at 185° C., all of the accelerators shown in Table I were recrystallized from alcohol. The purified products were found to have the following melting points: urea, 132° C.; thiourea, 168° C.; monophenylthiourea, 153° C.; diphenylthiourea, 151° C.; monophenylguanidine, 193° C.; *sym*-diphenylguanidine, 147° C.; triphenylguanidine, 143° C.

In the case of the substances shown in Table II, the *p*-phenylenediamine was recrystallized from alcohol and melted at 146° C. The anhydro-formaldehyde bodies possessed the following melting points: anhydro-formaldehyde aniline, 140° C. (with decom-

[1] THIS JOURNAL, 6 (1914), 514.
[2] Bureau of Standards, *Circular* 38 (1915), 66.
[3] This method was evolved and applied in the course of the present work, in order to overcome certain disadvantages in the Rosenstein-Davies method (*Chemist-Analyst*, 15 (1916), 4) previously employed.

position; monoanhydro-formaldehyde *p*-phenylenediamine, 142° C.: dianhydro-formaldehyde *p*-phenylenediamine, 192° C.

TABLE I—RELATIVE ACTIVITIES—THIOUREA SERIES
Parts Required to Equal One Part Aniline

Aniline	1.000
Urea	0.250
Thiourea	0.300
Monophenylthiourea	0.450
Diphenylthiourea	0.850
Monophenylguanidine (*a*)	0.075
Diphenylguanidine (*Sym*)	0.075
Triphenylguanidine	0.500

The activities of the various substances were compared in the mixture previously mentioned—92.5 parts of rubber and 7.5 parts of sulfur—taking as a standard[1] the effect obtained with one part of aniline, vulcanized for 90 min. at 148° C. The amounts of various substances in the urea series required to effect the same degree of vulcanization as obtained with one part of aniline are shown in Table I. The same is true for the anhydroformaldehyde aniline series, the results of which are shown in Table II.

TABLE II—RELATIVE ACTIVITIES—ANHYDRO-FORMALDEHYDE SERIES
Parts Required to Equal One Part Aniline

Aniline	1.00
Anhydro-formaldehyde aniline	0.76
p-Phenylenediamine	0.17
Monoanhydro - formaldehyde *p*-phenylenediamine	0.14
Dianhydro-formaldehyde *p*-phenylenediamine	0.14

As these preliminary tests were conducted solely to obtain information for guidance in subsequent experiments, and as no sulfur estimations were made, we do not feel warranted in drawing extensive conclusions from them. It would appear, however, that in the case of the urea series, the introduction of phenyl as a substituent for the hydrogen of the amido or imido group is responsible for a marked decrease in the activity of the parent substance. Also, in the case of the anhydro-formaldehyde series, it is evident that the introduction of the second amino group into the benzene nucleus increases the activity of the substance to a greater extent than substituting methylene for the hydrogen in the original amino group.

FINAL EXPERIMENTS—(1) This experiment was carried

[1] The comparisons were made at what was judged to be in each case the correct cure, as measured by the physical properties of the various mixtures only. Owing to this fact, the values assigned in Tables I and II were not found to be in strict agreement with their respective sulfur coefficients as determined in the subsequent experiments. Such comparisons, based on physical properties alone, are apt to be misleading, due to the toughening action imparted to the rubber when certain accelerators are employed; this effect is very noticeable in the case of *p*-phenylenediamine.

out in order to determine the relative accelerating effects produced by certain substances which contained hydroxyl or amino groups in their primary nucleus. Determinations were also made of the effect produced when the number, or kinds, of groups in the nucleus were altered or changed.

Every effort was made to obtain the various substances in the greatest degree of purity. Their physical constants were as follows: phenol, m. p. 41° C.; *p*-amidophenol, sublimed at about 180° C.; aniline, b. p. 185° C.; hydroquinone, m. p. 168° C.; *p*-phenylenediamine, m. p. 146° C.

The relative activity of these substances, as expressed by their sulfur coefficients, is shown in Table III.

TABLE III—RELATIVE ACCELERATION

First Latex Pale Crepe..... 92.5 parts
Sulfur ..... 7.5 parts
Accelerator ..... 1 part
Vulcanized for 90 min. at 148° C.

Added Substance	Combined Sulfur-Per cent	Sulfur Coefficient	Excess Sulfur Coefficient	Group Coefficient
Control	1.792	1.937	....	....
Phenol	1.689	1.779	—0.158	—0.00163
Hydroquinone	1.436	1.561	—0.376	—0.00170
p-Amidophenol	4.772	5.210	+3.273	....
Aniline	4.236	4.614	+2.677	+0.02870
p-Phenylenediamine[1] ...	7.286	7.955	+6.018	+0.02780

[1] As the combined sulfur obtained in this instance is so close to the total amount originally added to the mixture, this comparison was repeated with 0.25 per cent aniline and *p*-phenylenediamine. When employed in this amount, aniline gave an excess sulfur coefficient of 1.631 and *p*-phenylenediamine, 3.552. On calculation, their group coefficients were found to be 0.01630 and 0.01640, respectively.

From this table, it is seen that phenol, when expressed in terms of its sulfur coefficient, has a slight retarding influence which is almost exactly doubled in the case of hydroquinone, when the molecular weight of the latter is taken into consideration. Aniline and *p*-phenylenediamine are seen to exert a marked accelerating effect, as would be expected, and here, again, the effect produced by two amino groups is almost exactly twice that of a single group when the molecular weights of the two substances (aniline and p-phenylenediamine) are taken into consideration.[1] Thus, when equal weights of certain accelerators which contain active groups in the same primary nucleus are employed, it is possible to compare the activity of these groups *per se* by means of a group coefficient. Or, conversely, molecular quantities of substances which contain the same active group (or groups, if in equal number)

[1] The alkaloidal substances mentioned by Spence as decidedly active are undoubtedly of a high molecular weight.

in the primary nucleus should produce the same accelerating activity.

In the case of equal quantities by weight, this may be expressed as follows:

$$\text{Group coefficient} = \frac{Sx}{Mn}$$

where Sx = the excess sulfur coefficient over that of a control mixture vulcanized without an accelerator.

M = the molecular weight of the accelerator.

n = the number of the groups in the primary nucleus.[1]

When the results recorded in Table III are substituted in the above expression, the coefficient for the (OH) group is seen to be in good agreement for both phenol and hydroquinone; the same is true for the coefficients obtained for the (NH_2) group in both aniline and *p*-phenylenediamine. In other words, the introduction of a second group in the para position just doubles the activity. In light of our remarks in the introductory part of this paper, in regard to the function of these groups in accelerating the reaction between rubber and sulfur, we regard this point of much more importance than the numerical coefficient of the group itself, although a properly arranged table of group coefficients would undoubtedly be of value in anticipating the activities of untried substances.

II—In the previous experiment we employed substances of comparatively simple composition, and have attributed their action as accelerators to the presence of certain active groups. In the introductory part of this paper, however, we have pointed out that the action of certain other accelerators depends upon their ability to decompose, under vulcanizing conditions and temperatures, into degradation products containing an active group which is responsible for the acceleration effected. The present experiment was designed to further emphasize this point.

For this purpose, diphenylthiourea was chosen as the standard accelerator, on the assumption that

[1] The term "nucleus" is used as distinct from "molecule," in order to preclude the inclusion of similar groups in the side chains which, as Peachey has already noted, are not comparable in the effect produced. Likewise, as our work has been confined to two groups in the para position, further extension of this principle would require the introduction of another factor to compensate for the appearance of groups in the meta and ortho positions. In most cases, the ortho, meta and para products are increasingly active in the order named. Such differentiations, however, may be carried on indefinitely to include naphthylamines, etc. We have found β-naphthylamine to be almost twice as active as α-naphthylamine.

Table IV

First Latex Pale Crepe..... 92.5 parts
Sulfur ..... 7.5 parts
Accelerator ..... X parts
Vulcanized for 90 min. at 148° C.

	X = Parts Accelerator Added to the Mixture	Physical Properties	Odor of Cured Slab	Acetone Extract Per cent (Uncorrected)	Acetone Extract Per cent (Corrected)	Free Sulfur Per cent	Combined Sulfur Per cent	Total Sulfur Per cent (By Addition)
Control	0.00	1	Standard	8.630	2.894	5.736	1.792	7.528
Phenyl Mustard Oil.....	0.59	—1	Phenyl mustard oil	8.443	2.729	5.714	1.726	7.440
Aniline	0.41	4	Decomposition products of aniline	7.065	3.127	3.928	3.626	7.553
Phenyl Mustard Oil and Aniline	$C_6H_5NCS = 0.59$ $C_6H_5NH_2 = 0.41$	3	Phenyl mustard oil and decomposition products of aniline, the latter predominating	7.966	3.595	4.371	3.100	7.471
Diphenylthiourea	1.0	2	Phenyl mustard oil and decomposition products of aniline, the latter predominating	7.429	3.119	4.310	3.078	7.388
Diphenylthiourea and Aniline.	$(C_6H_5NH)_2CS = 1.0$ $C_6H_5NH_2 = 0.41$	6	Decomposition products of aniline predominating	7.301	3.963	3.338	3.959	7.297
Triphenylguanidine	1.25	6	Strong, but indistinguishable. Phenyl mustard oil could be detected	7.523	4.063	3.460	3.872	7.332

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Equation 1 is reversible and proceeds from right to left under the conditions and temperatures at which vulcanization ordinarily takes place.

Such being the case, and in view of the probable inactivity of phenyl mustard oil, the activity exerted by one part of diphenylthiourea should be no greater than that effected by a quantity of aniline corresponding to the amount required for the above reaction, when it is proceeding towards the left. Likewise, if the accelerating effect obtained with diphenylthiourea is dependent solely upon the amount of aniline formed by the decomposition of the former substance during vulcanization, the same should be true for triphenylguanidine, in accordance with Equation 2, which should also proceed from right to left during the vulcanization.

As mentioned in the introductory part of this paper, the diphenylthiourea and aniline formed undoubtedly undergo a subsequent decomposition with the formation of 2 molecules of aniline, and 1 molecule of phenyl mustard oil.

In order to test the above, our standard mixture was vulcanized for 90 min. at 148° C., with the assistance of one part of diphenylthiourea, and compared with similar mixtures which contained molecularly equivalent amounts of either one or both of the various decomposition products indicated in the above equations. The actual amounts of the different substances employed are shown in the second column of Table IV; they showed the following physical constants: phenyl mustard oil, b. p. 220° C.; aniline, 185° C.; diphenylthiourea, m. p. 151° C.; triphenylguanidine, m. p., 143° C.

Before any sulfur determinations were made, the different slabs were submitted to thumb and tooth tests in order that a rough estimation of their relative physical properties might be recorded. As shown in Table IV, the control has been used as the standard for comparison and given the number 1. The value 2, given to diphenylthiourea, simply indicates that it was faster than 1; number 3 was considered faster than 2, and so on for the rest of the series. The differences existing between the physical properties of the various slabs, however, were in no sense proportional to the numbers given them. The odor of the cured slabs was recorded in each instance and found to substantiate the preceding equations. The results obtained for the acetone extracts of the different mixtures, together with all the sulfur estimations made, are also recorded

in detail in Table IV. To facilitate comparison, the combined sulfurs, expressed as sulfur coefficients, are tabulated in Table V in the order of their relative magnitude.

TABLE V

First Latex Pale Crepe..... 92.5 parts
Sulfur ..... 7.5 parts
Accelerator ..... X parts
Vulcanized for 90 min. at 148° C.

Accelerator	Combined Sulfur Per cent	Sulfur Coefficient	Excess (+) Sulfur Coefficient
Phenyl Mustard Oil.....	1.726	1.877	—0.060
Control (No Accelerator).....	1.792	1.937	....
Diphenylthiourea	3.078	3.361	1.424
Phenyl Mustard Oil and Aniline....	3.100	3.385	1.448
Aniline	3.625	3.935	1.998
Triphenylguanidine	3.872	4.240	2.303
Diphenylthiourea and Aniline.....	3.959	4.340	2.403

From Table V it is seen that the sulfur coefficients obtained confirmed very closely the estimates made upon the physical properties. Further, it is shown that the activity of diphenylthiourea is almost exactly equal to that obtained with an amount of aniline corresponding to the quantity formed in its decomposition products as expressed in Equation 1. Likewise, triphenylguanidine was found to have the same activity as obtained with an equivalent amount of diphenylthiourea and aniline, as required by Equation 2, when the reaction proceeds toward the left.

It is evident that the action of both diphenylthiourea and triphenylguanidine as accelerators is due to their tendency to decompose, under vulcanizing conditions and temperatures, with aniline as one of the most probable degradation products. Moreover, it would appear that the aniline so formed is responsible for the acceleration effected, and owes its activity to the presence of an active group containing nitrogen, which functions as a sulfur carrier. That in no case were we able to recover the original amount of accelerator in the acetone extract, is an indication—and an indication only—that a portion of the active principle may also remain bound to the rubber as well as the sulfur.

Final emphasis is laid upon the fact that all of our results have been obtained with a mixture composed of rubber, sulfur, and accelerator only. The presence in the mixture of inorganic oxides has been found to have a marked influence on both the chemical and physical results obtained after vulcanization.

CONCLUSIONS

In view of the preceding results, we have been led to the following conclusions:

1—Comparisons of organic substances as accelerators should be made with molecularly equivalent amounts of the substances in question, and should be based on the values obtained for their excess sulfur coefficients over that of a control which contains no accelerator.

2—The action of certain substances, such as diphenylthiourea, is due to their tendency to decompose under vulcanizing conditions and temperatures into simpler substances which contain an active nitrogen group which is responsible for the acceleration effected.

3—Molecularly equivalent quantities of substances which contain the same active nitrogen group in their primary nucleus effect the same accelerating activity.

4—The replacement of the hydrogen in the active nitrogen group by other and larger groups, or radicals, decreases the activity of the parent substance.

5—The activity of the nitrogen in certain groups is most readily interpreted as due to a change in valency from three to five, with the temporary addition of sulfur; the active nitrogen group would thus function as a sulfur carrier.

845

V

The Republic Rubber Company

Factory and General Offices, Youngstown, Ohio.

Youngstown, Ohio,

December
First,
1 9 1 9.

IN REPLY PLEASE REFER TO _____

Defts Ex. No. V
U. S. Dist. Court,
S. D. of N. Y.
JAN 5
G Rel-23

Mr. George H. Stevens,
845 Broad St.,
Newark, N. J.

My dear Mr. Stevens:

In answer to yours of the 27th, I think that it would be wise to get your material together and come back at the end of this week, as I expect to be away from Thursday to Monday or Tuesday of next week. There will hardly be any time for further correspondence, therefore, please accept these instructions as final.

Very truly yours,

THE REPUBLIC RUBBER COMPANY

CHIEF CHEMIST.

P.S. on re-reading your letter, I'm not sure but that you are spending a little too much time on Triphenyl. Remember we are there only that. Diphenyl is the key pin now. Mark.

NHC-B

Defts. Exhibit F
Oct 8/25
H. M. C.

138

Defendnt's Exhibit F

DOVAN CHEMICAL CORPORATION

SYMMETRICAL DIPHENYLGUANIDINE

I. *Chemical Composition and Physical Properties.*

Symmetrical Diphenylguanidine $(C_6H_5NH)_2C:NH$ is a disubstituted guanidine and may be considered as thiocarbanilid in which the sulphur of the =C =S group has been replaced by the imid (=N=H) group.

Symmetrical Diphenylguanidine is a mono-acid base difficultly soluble in cold water, somewhat more soluble in boiling water. Its aqueous solution is strongly alkaline to phenol-phthalei It is soluble in practically all of the common organic solvents and is best re-crystallized from toluo in which it is very soluble in the hot but is almost insoluble in the cold.

The commercial material as offered by us to the rubber trade for use in accelerating th vulcanizing of rubber is a white, extremely finely divided powder, of a high degree of purity guaranteed to conform to the following specifications:

Melting Point	145-147° C.
(Chemically pure material melts at 147° C.)	
Ash	.3% Max.
Moisture	.3% Max.
Insoluble in dilute HCl	.2% Max.
Fineness	100% through 100 mesh
Color	Almost snow white

The impurities present consist of traces of ash and moisture and a small amount of organic impuri ties, the finished material assaying approximately 98.5% Diphenylguanidine. It is almost odorless is non-poisonous to workmen handling it in rubber manufacturing, and vulcanized articles containing it are odorless and free from all poisonous or objectionable fumes. This is particularly advantageous in all mechanical molded goods as it protects the health and increases the efficiency of the press or heater operator.

II. *Method of Handling Diphenylguanidine in the Factory.*

Since the material is a dry powder, and positively non-hygroscopic, no special methods of handling it are necessary, as it can be weighed as such and added directly to the batch to be mixed. Due to the extreme fineness of subdivision of Dovan Diphenylguanidine it disperses easily and completely in the rubber mix, thus insuring a uniform cure throughout the article.

If it is preferred to handle the material in the form of a master batch with rubber, 20 to 25% or even more can be very easily incorporated in the rubber. In mixing the master batch the rubber should be well masticated and then the DPG should be fed on slowly with a scoop, thus eliminating any tendency on the material to cake on the back roll. The final mix when cold is somewhat stiffer than crude rubber, and can be stored in any amount without fear of flowing together or deteriorating in any way.

III. *Characteristics of Diphenylguanidine as an Accelerator of Vulcanization.*

A. *Universal Applicability.*

Unlike nearly all other commercial available organic accelerators, diphenyl-guanidine can be used advantageously in all classes of rubber compounds, and in conjunction with all the known compounding ingredients. This is a very decided advantage, as it is not necessary to carry several accelerators in stock to use for special purposes, as is generally the case with other accelerators.

Defendant's Exhibit "G."

B. *Effects on Colors.*

Diphenylguanidine can be used in conjunction with practically all of the organic and inorganic colors without dulling or changing the tone in any way. This makes it very valuable for non-blooming inner tubes, drug sundries, etc., where a clean, bright color is essential.

C. *Critical Temperature.*

Although Diphenylguanidine is an exceeding active accelerator, its critical temperature is enough above the temperature attained on the calendar and mill to insure almost complete freedom from scorching. This makes it possible to compound very quick cure compounds, and is especially valuable for use in heavily compounded stocks such as tire treads, mechanical goods, drug sundries, and the like.

D. *Effect of Zinc Oxide.*

Although Diphenylguanidine is very active in a purely rubber-sulphur mix, zinc oxide is of assistance in producing its maximum accelerative effect. The maximum effect is produced by using five parts by weight of zinc oxide per 100 parts by weight of rubber. It is recommended that not less than three and preferably five parts by weight of zinc oxide be used per 100 parts rubber. Lime, magnesia and litharge activate Diphenylguanidine to some extent especially in hard rubber.

E. *Proportion of Sulphur to Rubber.*

Unless non-blooming stocks are required, the best stocks can be produced by using from 3 to 4 parts of sulphur to 100 parts of rubber. In general, it is best to use 3.5 parts sulphur per 100 parts rubber. This proportion gives a stock with a very flat curing curve, and insures good ageing qualities.

F. *Proportion of Accelerator to Rubber.*

Unlike many other accelerators, Diphenylguanidine is very active when present in very small amounts, and its activity increases almost proportionally to the increase of Diphenylguanidine up to about 0.75 parts per 100 parts of rubber. The best compounds are produced by using from 0.5 parts to 0.8 parts of Diphenylguanidine per 100 parts of rubber, using 3.5 parts of Sulphur.

G. *Ageing Qualities of Diphenylguanidine Compounds.*

Compounds accelerated with Diphenylguanidine age extremely well, especially when the proportion of sulphur to rubber is proper. Although it is recommended to use not over 3.5-4.0 parts of sulphur, stocks have been made having as much as 6.0-7.0% sulphur that aged very well. Here again Diphenylguanidine is shown to be a very advantageous accelerator, and one of wide applicability.

I. *Type Compounds for Various Rubber Articles.*

A. *Inner Tubes.*

1. *Gray—Light Bloom.*

Rubber	100.
Sulphur	3.5
Zince Oxide	5.
Diphenylguanidine	.6

Carbon Black or Lamp Black to suit.

This compound should be cured 30-35 minutes at 288° F. in open steam, depending upon the nature of rubber used. It is a lightly blooming tube, has excellent resistance to tear and ages extremely well. 0.5 to 1.0 parts cotton-seed oil may be added to decrease any tendency to check when exposed to light.

2. *Heavy Blooming Tube.*

Rubber	100.
Sulphur	5.
Zinc Oxide	5.
Diphenylguanidine	.125

This stock should be cured 40-45 minutes at 288° F. It is a heavy blooming tube, but ages very well.

3. *Non-blooming Colored Tubes.*

Rubber	100.
Sulphur	2.5
Zinc Oxide	5.
Diphenylguanidine	.75

To the above mixture may be added carbon black, red oxide, golden or crimson antimony free from free sulphur, or any of the organic colors to produced desired shade. The above should be cured about 60 minutes at 288° F. to be non-blooming. The physical properties and aging qualities are very good and colors are particularly clear.

Tire Compounds.

1. *Friction, skim coat, cover stocks, etc.*

The following type compound can be used to produce high rubber stocks of any cure desired.

Rubber	100.
Sulphur	3.5 to 4.0
Zinc Oxide	5. to 25.
Diphenylguanidine	.4 to 0.75

If the following recipe be used:

Rubber	100.
Zinc Oxide	5.
Sulphur	3.75
Diphenylguanidine	0.75

the best technical cure is from 30 to 35 minutes at 288° F.

To the above can be added Mineral Rubber, Softeners and Fillers to suit.

2. *Sidewall Stocks.*

Rubber	65.
Sulphur	2.25
Zinc Oxide	30.
Diphenylguanidine	.3
Color to Suit.	

3. *Tread Stocks.*

Rubber	92.5 = 100 vol.
Sulphur	3.5
Diphenylguanidine	.75 to 1.0

To the above may be added the necessary pigments to obtain rigidity desired. The cure will depend entirely upon what compounding ingredients are added, and their amounts, as some materials retard a great deal, others slightly, others are neutral, and some are slightly accelerative.

Cure on the above type compounds with 5 to 10 parts Zinc Oxide added to activate the Diphenylguanidine is 30 minutes at 288° F.

Using 20 vol. Carbon Black, Cure = 45 to 70 minutes at 288° F., depending on brand used.

Barium Sulphate, Whiting, Lithopone and Aluminum Flake are Neutral, curing in 30 minutes at 288° F.

China Clays retard slightly, curing in 40 to 45 minutes at 288° F.

4. *Hard Rubber.*

Diphenylguanidine is an exceedingly valuable accelerator for hard rubber goods. It has great curing power and is odorless. Heavily loaded stocks can be milled without danger of scorching. The texture of hard rubber produced with Diphenylguanidine is unequalled.

5. *Dry Heat Compound.*

Diphenylguanidine also will give excellent results in dry heat cures. It will replace litharge and give comparable results with a shorter cure. In addition, it can be used in light colored stocks. It is recommended to use 1.5-2.0% of Diphenylguanidine and 2.5-3.0% of Sulphur. The time of cure will depend on the rapidity of the rise and on the temperature.

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6. *Molded Goods.*

The use of Diphenylguanidine is very advantageous for many reasons. It is universally applicable to all sorts of compounds and shows high curing power in presence of reclaimed rubber and every sort of cheap compounding material, such as mineral rubber, resins, pitches, waxes, etc. Most important of all in this class of goods is the fact that no unpleasant fumes are given off from the hot goods when the molds are opened, which protects the workman and increases his efficiency:

Following is a type formula for heel stocks:

Rubber	25.
Reclaim (Tire)	25.
Sulphur	1.25 to 1.5
Diphenylguanidine	.5 to .6
Zinc Oxide	10.
Carbon Black or Red Oxide..	5.
Clay	30.
Softener	1.25

Cure: 10 to 15 minutes at 65 to 70 lbs. steam pressure.

SUMMARY:

The advantages of Diphenylguanidine are:

1. Non-poisonous to handle, odorless and free from all objectionable fumes.
2. No special means of handling are necessary, as it is a finely divided, dry, non-hygroscopic powder.
3. It is applicable to every class of rubber compound.
4. Works in conjunction with all compounding ingredients.
5. Very active in presence of reclaimed rubber.
6. Does not dull or destroy organic colors.
7. If the sulphur to rubber proportion is proper, the stocks have a long flat curing curve and are therefore foolproof.
8. Its critical temperature is high enough to prevent scorching.
9. It is very active, even in very low percentages.
10. Properly compounded, stocks age extremely well, and have very little tendency to overcure.
11. Produces non-blooming stocks of very good qualities.
12. Produces pure gum compounds with a very high resistance to tear, therefore valuable in tube stocks.
13. Does not lose its curing power on being stored or when milled into compounds, no matter how long they are kept.
14. Low specific gravity—being less than 1.
15. It has a basic reaction and therefore keeps the rubber in vulcanized compounds in a non-polymerized state which is most conducive to good ageing.

SE IN CENTER

Defendant's Exhibit "H."

File wrapper of patent in suit.
(Consisting of 68 pages)

851

NUMBER (Series of 1915).
514 727

1921

(EX'R'S BOOK) 145-2

DIV. 15

PATENT No. 1411231

MAR 23 1922

Name Morris L Kerr
Assor to Dovan Chemical Corporation of Wilmington, Del. a corp of Delaware

of Brooklyn.

County of

State of New York

Invention Vulcanization Accelerator

	ORIGINAL	RENEWED
Petition	Nov. 12, 1921	, 19
Affidavit	" " , 1921	, 19
Specification	" " , 1921	, 19
Drawing	, 19	, 19
Photo Copy	, 19	, 19
First Fee Cash $15	Nov. 12, 1921	, 19
" " Cert.	, 19	, 19
Appl. filed complete	Nov. 12, 1921	, 19
(Signed) W. L. Redman	Oct 28, 1922	
Examined and Passed for Issue	Feb 14, 1922	, 19
(Signed) W. L. Redman	Exr. Div. 15	
Notice of Allowance	Feb 15, 1922	, 19
Final Fee Cash $20	Feb 17, 1922	, 19 2
" " Cert.	, 19	, 19
Patented		, 19

Attorneys Sheffield & Betts, 52 William St, New York City

Associate Attorney

(No. of Claims Allowed 12) (Print Claim) in O. G. (Cl. 18-53)

Title as Allowed Vulcanization Accelerators

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Sig. 2.

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JAMES F. SHEFFIELD
L. P. M. BETTS
JOHN W. PETERS
JAMES J. OSBORNE
EDWARD W. VAILL
ABEL E. BLACKMAR, JR.

SHEFFIELD & BETTS
COUNSELLORS AT LAW
52 WILLIAM STREET
New York

SAMUEL A. BETTS
COUNSEL

November 10th, 1921.

Hon. Commissioner of Patents,
Washington, D. C.

Sir:-

We are enclosing herewith for filing an application of Morris L. Weiss for improvements in "Vulcanization Accelerators", together with our check for $15.00 to cover the cost of filing said application.

Respectfully,

Sheffield & Betts

JH.

Enclosure.

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appln

PETITION AND POWER OF ATTORNEY

To the Honorable Commissioner of Patents:

Your Petitioner MORRIS L. WEISS

a Citizen of the United States of America,

Residing in Brooklyn, County of Kings, State of New York

and whose Post Office Address 2812 Church Ave., Brooklyn, N. Y.

respectfully prays that Letters Patent of the United States of America may be granted to your petitioner for the improvements in

VULCANIZATION ACCELERATORS

set forth in the annexed specification, and your petitioner hereby appoints James R. Sheffield, Louis Frederic Holbrook Betts, John W. Peters, James J. Cosgrove, Edward W. Vaill and Abel E. Blackmar, Jr., composing the firm of Sheffield and Betts, of No 52 William Street, Borough of Manhattan, in the City and State of New York, Attorneys at Law, whose registration number is 3902, or their accredited agent or agents, as attorneys in the premises, with full powers of substitution and revocation, to prosecute this application, to sign the drawings, to make and sign alterations and amendments, to receive the letters patent when granted and to transact all business in the Patent Office connected with said application.

Morris L Weiss

~~SPECIFICATION~~

TO ALL WHOM IT MAY CONCERN:

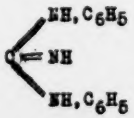
BE IT KNOWN that I, MORRIS L. WEISS, a citizen of the United States, residing in the Borough of Brooklyn, County of Kings, City and State of New York, have invented certain new and useful improvements in

VULCANIZATION ACCELERATORS,

of which the following is a full, clear, concise, and exact description.

The object of my invention is to improve rubber compounds so that the finished product shall be of superior quality and so that the time required for vulcanization shall be greatly reduced over that ordinarily required for such purpose. It is known that when certain organic substances are added to the rubber mix during the compounding, a catalytic or similar action is produced which causes the rubber or similar gum to unite or react more rapidly and thoroughly with sulphur or other vulcanizing agents.

I have discovered that disubstituted guanidines particularly diphenylguanidine is particularly effective for this purpose. This substance is indicated by the formula



I am aware that disubstituted guanidines have been produced by laboratory methods and have been known to chemists for many years beginning about the year 1868

with the work of A. W. Hoffman (An. Chem. Parm. 67:129), but down to time of my researches in accelerators of this type, it was apparently not known that di-substituted guanidines were efficacious or useful as accelerators in vulcanizing, nor that this substance could be produced in sufficiently large quantities in a substantially pure form, or at a sufficiently low cost to be available for this purpose.

I am aware that triphenylguanidine has been suggested, and probably used to some extent, as an accelerator in the vulcanization of rubber, but the use of diphenylguanidine for that purpose appears to have been unknown prior to my researches on this substance.

I have found that diphenylguanidine is much more powerful and efficacious as an accelerator in vulcanization than triphenylguanidine. For example, in the vulcanization of hard rubber articles the use of diphenylguanidine not only hastens the vulcanizating action but results in a final product much superior in texture, strength, durability and aging qualities over that when the triphenylguanidine is used. A greatly improved product also results when diphenylguanidine is used as an accelerator in the vulcanization of soft rubber compounds, particularly as regards elasticity, aging qualities and freedom from "bloom". In these and similar instances, it has been found that the use of triphenylguanidine requires from two to three times as long a period in vulcanizing as when diphenylguanidine is used, particularly at lower heat or steam pressures than those commonly employed.

In my prior application Serial No. 482,143

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filed July 2, 1921, I have described and claimed a proces for producing and purifying diphenylguanidine in commerci quantities, and have therein given a resume of the histor cal development of the methods of producing the same.

As set forth in said application, I, at present prefer to produce my improved accelerator by desulphuriz thiocarbanilide by the action of a metallic oxide, such a lead oxide, zinc oxide, etc., in an alcoholic solution of an ammonium salt, such as ammonium nitrate.

The present patent application therefore relate to the vulcanization of rubber or similar substances, in which disubstituted guanidines are employed as the accele ating agent or catalyzer, and particularly diphenylguanid

The method of carrying out my invention, which at present deem preferable, may be illustrated by the fol lowing example:

The rubber may be compounded in the following propor tions: 50 ~~.00~~ parts by weight of new rubber,
45.5 " " " " zinc oxide,
3.5 " " " " sulphur,
1 ~~.00~~ part " " " diphenylguanidine.

These are mixed together in any suitable way, such as by milling, and then vulcanized or cured in the usual molds or otherwise under heat corresponding to a steam pressure of about 40 lbs. per square inch. This vul canizing temperature should be continued until the compou is suitably vulcanized, which requires from 10 to 20 minut depending upon the shape and size of the articles being vulcanized.

It will therefore be appreciated that when usin the accelerator according to my invention the vulcanizati

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is accomplished by using comparatively small quantities of the accelerator, thereby obviating undesirable loading or adulteration of the rubber compound. Furthermore, by the use of such accelerator, the texture and durability of the final product is greatly improved and the tendency commonly present in vulcanized rubber to bloom and become brittle with age is greatly reduced if not entirely obviated. My improved accelerator is particularly useful and valuable where it is desired to produce a harder or less elastic portion in an article leaving other parts which are reqdred to be more elastic and flexible, such as in automobile tires where the beadstock is usually made harder than the body or carcass of the tire proper. The relative amounts of vulcanizing agent and accelerator may be so proportioned that the various parts or a single article may be cured to different degrees of hardness without danger of over-curing the softer or more elastic parts. I have found moreover than diphenylguanidine does not need zinc oxide to shorten the time of cure. I however prefer to use zinc oxide on account of its effects on the physical properties of the product.

Having thus described this example of my invention and the method of using the same, I do not wish to be understood as being limited to the exact proportions, ingredients, temperatures, etc., indicated, for various changes may be made without departing from the essential features of my invention as set forth in the accompanying claims.

What I claim and desire to protect by Letters Patent is:

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1. The process of treating rubber or similar materials, which comprises combining with the rubber compound a di-substituted guanidine.

2. The process of treating rubber or similar materials which comprises combining with rubber compound a di-substituted guanidine comprising two phenyl radicles or groups.

3. The process of treating rubber or similar materials which comprises combining with the rubber compound an accelerator derived from thiocarbanilide in which the sulphur is substituted by an imide group.

4. The process of treating rubber or similar materials which comprises combining with the rubber compound diphenylguanidine.

5. The process of treating rubber or similar materials which comprises combining with the rubber compound a vulcanizing agent and a di-substituted guanidine accelerator.

6. The process of treating rubber or similar materials which comprises combining with the rubber compound a vulcanizing agent and a di-substituted guanidine comprising two phenyl radicles or groups.

7. The process of treating rubber or similar materials which comprises combining with the rubber compound a vulcanizing agent and an accelerator derived from

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thiocarbanilide in which the sulphur is substituted by an imide group.

8. The process of treating rubber or similar materials, which comprises combining with the rubber compound a vulcanizing agent and diphenylguanidine.

9. A vulcanizing compound of rubber or similar material combined with a vulcanizing agent and a di-substituted guanidine.

10. A vulcanized compound of rubber or similar material combined with a vulcanizing agent and di-substituted guanidine comprising two phenyl radicles or groups.

11. A vulcanized compound of rubber or similar material combined with a vulcanizing agent and an accelerator derived from thiocarbanilide in which the sulphur is substituted by an imide group.

12. A vulcanized compound of rubber or similar material combined with a vulcanizing agent and diphenylguanidine.

Signed at New York, N. Y.,
November 10th, 1921.

Morris L. Weiss

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AFFIDAVIT

STATE OF NEW YORK }
COUNTY OF NEW YORK } ss.:

MORRIS L. WEISS

the above-named petitioner, being sworn, deposes and says that he is a citizen of the United States of America,

and resident of the Borough of Brooklyn, County of Kings, City and State of New York,

that he verily believes himself to be the original, first, and sole inventor of the improvements in VULCANIZATION ACCELERATORS

described and claimed in the annexed specification; that he does not know and do as not believe that the same was ever known or used before his invention or discovery thereof, or patented or described in any printed publication in any country before his invention or discovery thereof, or more than two years prior to this application, or patented in any country foreign to the United States on an application filed by him or his legal representatives or assigns more than twelve months before this application, or in public use or on sale in the United States for more than two years prior to this application; and that no application for patent on said improvements has been filed by him or his legal representatives or assigns in any country foreign to the United States.

Morris L. Weiss

Sworn to and subscribed before me this
10th day of November, 192

Walter S. Jones
Notary Public,
New York County.

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Dr. 15 Room 308 — 2-200 — Page No. 2

Address only "The Commissioner of Patents, Washington, D.C." and not by official by name.

H/MEY

All communications relative to securing this application should give the serial number, date of filing, name of inventor, and name of the applicant.

DEPARTMENT OF THE INTERIOR

UNITED STATES PATENT OFFICE

WASHINGTON Dec. 29,1921

Sheffield and Betts

52 William St.

New York, N.Y.

Please find below a communication from the EXAMINER in charge of the application of

M.L.Weiss,Ser.No.514,727,filed Nov.12,1921; Vulcanization Accelerators.

Thomas E. Robertson

Commissioner of Patents.

This case has been examined.

The claims are rejected on

India Rubber World May 1,1921 page 372- second column 3rd paragraph line 4 "Diphenylguanidine".

The India Rubber World is published in New York by Henry C Pearson.

A new oath is required, the present one being dated Nov.10,192

A. V. Chandler

act. Examiner.

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IN THE UNITED STATES PATENT OFFICE

In re Application of

MORRIS L. WEISS

Serial No. 514,727 Division 15 - Room 308

Filed November 12, 1921

VULCANIZATION ACCELERATORS

New York, N. Y., January 3, 1922

TO THE HONORABLE COMMISSIONER OF PATENTS

Washington, D. C.

S i r :

Official action of December 29, 1921, received. The rejection of the claims on the publication in the India Rubber World of May 1, 1921, is noted. It is also noted that said publication refers to a paper read at the meeting of the American Chemical Society in Chicago, September 6-10, 1920. In view of this latter date, which purports to mention the use of the accelerator of this application in September, 1920, the affidavits herewith submitted under Rule 75 of the Rules of Practice have been drawn to ante-date said latter date of September 6, 1920, instead of May 1, 1921, the actual date of the publication and the one legally effective as a publication under the statutes. Therefore, the accompanying affidavits of Morris L. Weiss, the inventor, and Henry S. Doty, President of the assignee company, the Dovan Chemical Corporation, are herewith submitted, which clearly show not only

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reduction to practice, but the marketing of the accelerator involved in this application prior to September 6, 1920.

It is thought that these affidavits now put this case in condition for allowance. In view of applicant's copending allowed case involving the process of making this accelerator, it is requested that this case be taken up for action and allowance at the earliest possible date in order that these two cases may issue together to avoid any question of conflict between them.

A new oath is submitted herewith, as required, although the applicant's file copy of the same indicates that the date of execution is complete.

Very respectfully

MORRIS L. WEISS

By Shuffred & Betts.

his Attorneys.

IN THE UNITED STATES PATENT OFFICE

In re Application of

MORRIS L. WEISS

Serial No. 514,727 — Division 15 - Room 808

Filed November 12, 1921

VULCANIZATION ACCELERATORS

- AFFIDAVIT OF MORRIS L. WEISS -

STATE OF NEW YORK)
(SS.:
COUNTY OF NEW YORK)

MORRIS L. WEISS, being duly sworn, deposes and says as follows:

I am the applicant named in the above entitled application, Serial No. 514,727, filed November 12, 1921. I am a chemist employed by the Dovan Chemical Corporation, assignee of said application. The invention, which is the subject matter of the claims, was conceived, disclosed to others and reduced to practice by me prior to September 6, 1920, and said reduction to practice comprised the actual use of diphenylguanidine as an accelerator in the vulcanization of rubber articles.

FURTHERMORE, said diphenylguanidine was placed on the market for use by manufacturers of rubber goods by the predecessors of said Dovan Chemical Corporation prior to September 6, 1920.

I also depose and say that I do not know and do not believe that said invention has been in public use or on sale in the United States or patented or described

in a printed publication in the United States or any foreign country for more than two years prior to my said application and that I have never abandoned the said invention.

Morris L. Weiss

Sworn to before me this 3rd day of January, 1922.

Walter S. James
Notary Public
New York Co.

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IN THE UNITED STATES PATENT OFFICE

In re Application of

MORRIS L. WEISS

Serial No. 514,727 — Division 15 - Room 308

Filed November 12, 1921

VULCANIZATION ACCELERATORS

- AFFIDAVIT OF HENRY S. DOTY -

STATE OF NEW YORK)
(SS.:
COUNTY OF NEW YORK)

HENRY S. DOTY, being duly sworn, deposes and says as follows:

I am President of the Dovan Chemical Corporation, assignee of the application of Morris L. Weiss, Serial No. 514,727, filed November 12, 1921, for vulcanization accelerators. To my personal knowledge, the invention stated in the claims of said application was disclosed to me, reduced to practice and successfully used by said Morris L. Weiss prior to September 6, 1920.

FURTHERMORE, diphenylguanidine made in accordance with the specification and claims of said application was put on the market by the predecessors of said Dovan Chemical Corporation and was delivered to manufacturers of rubber goods as an accelerator for use in rubber vulcanization prior to September 6, 1920.

Henry S. Doty.

Sworn to and subscribed before
me this 4th day of January, 1922.

Walter D. Jones.
Notary Public
New York Co.

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AFFIDAVIT

STATE OF NEW YORK }
COUNTY OF NEW YORK } ss.:

MORRIS L. WEISS

the above-named petitioner, being sworn, deposes and says that he is a citizen of the United States of America, and resident of Borough of Brooklyn, County of Kings, City and State of New York; that he is the applicant named in application Serial No. 514,727, filed November 12, 1921, that he verily believes himself to be the original, first, and sole inventor of the improvements in VULCANIZATION ACCELERATORS described and claimed in the said application; that he do es not know and do es not believe that the same was ever known or used before his invention or discovery thereof, or patented or described in any printed publication in any country before his said invention or discovery thereof, or more than two years prior to his said application, or patented in any country foreign to the United States on an application filed by him or his said legal representatives or assigns more than twelve months before his said application, or in public use or on sale in the United States for more than two years prior to his said application; and that no application for patent on said improvements has been filed by him or his said legal representatives or assigns in any country foreign to the United States.

Morris L. Weiss

Sworn to and subscribed before me this 3rd day of January, 1922

Walter S. Jones
Notary Public,

New York County.

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Div. 15 Room 308 2-868 Paper No. 4

Address only "The Commissioner of Patents, Washington, D.C." and not any official by name.

All communications concerning this application should give the serial number, date of filing, title of invention, and name of the applicant.

H/MFY

DEPARTMENT OF THE INTERIOR

UNITED STATES PATENT OFFICE

WASHINGTON Jan.13,1922

Sheffield and Retts

52 William St.

New York, N.Y.

Please find below a communication from the EXAMINER in charge of the application of

Morris L Weiss,Ser.No.514,727,filed Nov. 12,1921;

Vulcanization Accelerators.

Thomas E. Robertson

Commissioner of Patents

In response to letter of Jan.6,1922

The affidavit filed under Rule 75 is not sufficiently specific as to the facts presented therein.

Merely stating that the invention was disclosed to others before Sept. 6,1920 and reduced to practice - does not bring out all the facts in applicant's possession To whom was it disclosed and when? When was it placed on the market and where? There must be a completion of the invention in this country before the date of the reference. Furthermore a public address before the American Chemical Society disclosing completely the invention on Sept. 6,1920 shows knowledge which applicant must overcome by bringing his dates back of Sept.6, 1920.

The new oath under Rule 46 has been filed and accepted.

The affidavit under Rule 75 is rejected, and the claims stand rejected.

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M. L. Reams

IN THE UNITED STATES PATENT OFFICE.

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#5

In re Application of : Division 15, Room 308.

MORRIS L. WEISS, :

Serial No. 514,727; : VULCANIZATION ACCELERATORS

filed November 12, 1921.:

- - - - - - - - - - - - - -

New York, January 19, 1922.

HON. COMMISSIONER OF PATENTS,

Washington, D. C.

Sir:-

The Official action of January 13, 1922, received. In accordance with said Official action, additional affidavits are submitted herewith, said affidavits having been executed by the inventor, Morris L. Weiss, and Henry S. Doty and Chester Frankenstein. It is thought that these affidavits now fully set forth the specific facts and include the dates and location of the same. Said affidavits clearly anticipate the date of September 6, 1920, mentioned by the Honorable Examiner, and therefore invalidate the reference to the India Rubber World cited in the previous Office action. In view of this, it is thought that the application is now in condition for allowance, and in view of applicant's co-pending allowed application serial No. 482,143, filed July 2, 1921, for a process for producing and purifying diphenylguanidine, it is requested that early action be taken in this case, for

the reasons previously set forth. Said prior application is mentioned in the specification herein at the bottom of page 2 and at the top of page 3.

Early and favorable action is solicited.

Very respectfully,

MORRIS L. WEISS,

By Shumway & Sells
his Attorneys.

IN THE UNITED STATES PATENT OFFICE.

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In re Application of : Division 15; Room 308.

MORRIS L. WEISS, :

filed November 12, 1921;: VULCANIZATION ACCELERATORS.

Serial No. 514,727. :

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AFFIDAVIT OF MORRIS L. WEISS.

State of New York,)
: ss.:
County of New York)

MORRIS L. WEISS, being duly sworn, deposes and says as follows:

I am the applicant named in the above entitled application serial No. 514,727, filed November 12, 1921. I am a chemist employed by the Dovan Chemical Corporation, assignee of said application. The invention which is the subject matter of the claims thereof was conceived by me prior to January 1, 1920.

On or about the 7th day of April, 1920, I called at the office of Mr. Henry S. Doty and Mr. Van Lear Woodward, at 30 Church Street, New York City, and disclosed to them the said invention, and also delivered to them, at said time and place, a sample of diphenylguanidine which I had previously prepared for use as an accelerator in rubber vulcanization. I then and there explained to them the purpose and manner of its use. Said Doty and said Woodward agreed to make a test of said invention using said sample as an

accelerator for rubber vulcanization, and accordingly tests were conducted by said Doty at the laboratories of the States Metals Company at Long Island City, New York. on or about April 8th, 1920. I was thereafter informed, within two or three days, by said Doty and said Woodward that said tests had been made and were considered by them to clearly demonstrate the success, value and practicability of said invention.

Thereupon it was mutually agreed between said Doty, said Woodward and the deponent that they should co-operate with each other in placing said diphenylguanidine on the market as an accelerator for rubber vulcanization.

Preparations for the manufacture of diphenylguanidine in commercial quantities was then begun and during the period from May, 1920, to September, 1920, about one hundred and fifty pounds of diphenylguanidine had been manufactured at the laboratories equipped for that purpose and located at 980 East 35th Street, Brooklyn, New York, by said Doty and Woodward and the deponent.

During the month of August, 1920, various rubber goods manufacturing concerns were advised by letters of the availability of diphenylguanidine as an accelerator for rubber vulcanization, and beginning about the last week in August, 1920, samples of the same were sent to a number of rubber goods manufacturers, including the General Tire and Rubber Company, of Akron, Ohio, and New Castle Rubber Co., New Castle, Pa.

Sales of said accelerator were begun about the latter

part of September, 1920, and have been continued by said Doty, Woodward and the deponent and by the States Metals Company as the distributing organization of the Dovan Chemical Corporation, the assignee of the present application, which corporation succeeded said Doty and Woodward and the deponent as manufacturers thereof. The manufacture and sale of said accelerator was thereafter continued without interruption until the present date except for a period of several weeks when the factory or laboratories of the Dovan Chemical Corporation in Brooklyn, New York, was destroyed by fire, and a new factory put in operation at Newark, New Jersey

I also depose and say that I do not know and do not believe that said invention has been in public use or on sale in the United States or patented or described in any printed publication in the United States or in any foreign country more than two years prior to my said application, and I have never abandoned said invention.

M. L. Weiss
Morris L. Weiss

Sworn to and subscribed before me this 27th day of January, 1922.

Walter S. Lewis.
Notary Public,
New York Co.

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IN THE UNITED STATES PATENT OFFICE.

- - - - - - - - - - - - - - -

In re Application of : Division 15; Room 306.

MORRIS L. WEISS, :

filed November 12, 1921; : VULCANIZATION ACCELERATORS

Serial No. 514,727. :

- - - - - - - - - - - - - - -

AFFIDAVIT OF HENRY S. DOTY.

State of New York,)
: ss.:
County of New York)

HENRY S. DOTY, being duly sworn, deposes and says as follows:

I am President of the Dovan Chemical Corporation, assignee of the above mentioned application.

On or about April 7, 1920, Morris L. Weiss called at my office, 30 Chruch Street, New York City, and disclosed to myself and Van Lear Woodward the invention set forth in said application. Said Weiss also delivered to me at said time and place a sample of diphenylguanidine and explained to me and said Woodward the manner and method of using the same in the vulcanization of rubber articles. Thereupon deponent agreed to make tests of said sample and on or about April 8 said tests were conducted by the deponent at the laboratories of the States Metals Company at Long Island City, New York. The deponent was assisted in said tests by Chester Frankenstein. These tests were made by introducing said accelerator

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into so-called "tread stock" for automobile tires and then vulcanizing the same. Parallel tests were also conducted at the same time using hexamethylene tetramine in the same proportions as an accelerator. The results of said tests showed that diphenylguanidine was much superior to hexamethylene-tetramine as an accelerator.

During the month of June, 1920, the deponent made a series of tests at said laboratories using diphenylguanidine as an accelerator and also compared the same with the action of hexamethylene tetramine. A report of said test was made on or about June 15, 1920, a copy of which is attached hereto marked "Exhibit A". Both of said tests demonstrated to me the success, practicability and value of said invention. After the test of April, 1920, said Weiss and Woodward and the deponent agreed to co-operate in the manufacture and sale of diphenylguanidine as an accelerator. Preparations were then made for the manufacture of the same in commercial quantities.

During the month of June, 1920, sufficient quantities of chemicals were purchased by said Weiss and Woodward and the deponent to start the manufacture of said accelerator. Copies of invoices for said chemicals are attached hereto and marked "Exhibit B". Thereafter, from June, 1920, to September 1920, about one hundred and fifty pounds of the same were manufactured at laboratories equipped for that purpose at 980 East 35th Street, Brooklyn, New York.

During the month of August, 1920, various rubber goods manufacturing concerns were advised of the availability of diphenylguanidine as an accelerator for rubber vulcanization through letters sent to said concerns. Copies of such letters are attached hereto as "Exhibit C". In this "Exhibit C" references to "XLO" refer to the accelerator comprising diphenylguanidine as the active ingredient thereof. Beginning about the last week in August, 1920, samples of the same were sent to various manufacturers of rueber goods, including the General Tire and Rubber Company, of Akron, Ohio, and Goodyear Tire & Rubber Company, Akron, Ohio, and others.

Sales of said accelerators were begun about the latter part of September, 1920, and were made to various rubber manufacturing concerns, including the Dunlap Tire & Rubber Company of America, Buffalo, New York, and the Mason Tire & Rubber Company, at Kent, Ohio, and others.

H&B See order of Exhibit D"

Said sales were continued by said Weiss, Woodward and the deponent and by the States Metals Company as distributing organization for them and for the subsequently incorporated Dovan Chemical Corporation, which manufactured said accelerator as successor of said Weiss, Woodward and deponent Said manufacture was carried on continuously at the factory and laboratories of Dovan Chemical Corporation and their said predecessors, which factory and laboratories were located at Brooklyn, New York, until destroyed by fire on or about September 8, 1921, said manufacture being then interrupted for several weeks until the equipment of a new factory at Newark, New Jersey, was completed, where said manufacture has since

been continued.

Henry S. Doty.

Sworn to and subscribed before
me this 17th day of January,
1922.

Walter S. Jones.
Notary Public,
New York Co

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EXHIBIT A

LABORATORY REPORT

New York, June 15, 1920.

File Accelerator Tests

Test No. Made by Checked by H.S.D.

Sample of Diphenylguanidine

From M. L. Weiss

Reference Compare accelerative action vs. Hexamethylene Tetramine.

Tested in See below * compound. Laboratory recipe No. ---

Cure	15min @ 40#		25min @ 40#		35min @ 40#		50min @ 40	
~~Specific Gravity~~	Hexa	DPG	Hexa	DPG	Hexa	DPG	Hexa	DPG
Tensile strength per sq. inch	1432	2702	2424	3040	2718	3646	3054	344
Elongation at break	660%	580%	610%	560%	600%	540%	550%	510%

Permanent Set

[One inch sample stretched to inches for 10 minutes, released, and measured after 10 minutes rest period.]

REMARKS-

Smoked Sheets	Plantation Rubber	50%
	Zinc Oxide	46-3/4%
	Sulphur	3-1/2%
	Accelerator	3/4%

(Weight of Diphenylguanidine in the "D.P.G." compound exactly equal to weight of Hexamethylene Tetramine in "Hexa" compound in order to get comparative accelerative action.)

HSD/M

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TELEPHONE, HANOVER 5696

NEW YORK, N. Y., JUNE 21st, 1920.

Mr. M. L. Weiss, % Frazar Co., 30 Church St., New York City, N. Y.

To L. PLASS COMPANY, Dr.

130 PEARL STREET

TERMS: Net cash. PAYABLE IN NEW YORK EXCHANGE

1 drum CAUSTIC SODA 76% GROUND

523 lbs. net at 6-3/4¢ per lb. $35.30

541-18-523 lbs.

Shipped to-

H. E. Winfield-
980 East 35th St.,
Brooklyn- N. Y.

I Rec'd

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ALL CLAIMS MUST BE MADE WITHIN TEN DAYS FROM RECEIPT OF GOODS.

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EXHIBIT B (.)

TELEPHONE, HANOVER 5666

NEW YORK, N. Y., JULY 21st, 1920.

880

Mr. M. L. Weiss, & Frazar Co., 30 Church St., New York City, N. Y.

To L. PLASS COMPANY, Dr.

130 PEARL STREET

TERMS: Net Cash. PAYABLE IN NEW YORK EXCHANGE

2 drums of ANILINE OIL

45 - 1028 - 183 - 845
45 - 1037 - 207 - 830

1675 lbs. Net @ 35¢ per lb.	$586.25
DRUMS extra and returnable	50.00
	$636.25

~~636.25~~

Shipped to-

H. E. Winfield,
960 East 35th St.,
Brooklyn, N. Y.

ALL CLAIMS MUST BE MADE WITHIN TEN DAYS FROM RECEIPT OF GOODS.

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McKESSON & ROBBINS

NEW YORK, N.Y.

United States License
No. 24888
Food Administration

NE 16TH 1920 Your Order Salesman

M L WEISS
C/O A.C. WINFIELD
980 E 35TH ST.
BROOKLYN. N.Y.

Invoice Date
JUNE 16TH 1920
Book
615 029
Terms
C O D

Remarks

Payable in Gold or its equivalent, in NEW YORK or sight exchange.

UMS	CARBON BI_SULPHIDE	ABOUT 1000LBS	09	90.00
		2 DRUMS	15.00	30.00
				120.00

TO BE DELIVERED W THIN A WEEKS TIME.

MGM/

— Bills not paid within 30 days will be subject to draft with exchange on New York. We cannot guarantee the safe delivery of ...obtaining a receipt for same, as "Shipped in Good Order," we are not responsible for any damage or loss that may occur in transit... claims allowed unless date of our invoice is given. All claims must be made within 5 days after receipt of goods. Should you ...to refer to this invoice, please mention Book Number as given above.

...ense the merchandise entered herein manufactured by [illegible] to comply with the Federal Food and Drugs Act and Amendments thereto.

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IN THE UNITED STATES PATENT OFFICE.

- - - - - - - - - - - - - - -

In re Application of : Division 15; Room 308.

MORRIS L. WEISS, : VULCANIZATION ACCELERATORS

filed November 12, 1921; :

Serial No. 514,727. :

- - - - - - - - - - - - - - -

AFFIDAVIT OF CHESTER FRANKENSTEIN.

State of New York,)
: ss.:
County of New York)

CHESTER FRANKENSTEIN, being duly sworn, deposes and and says as follows:

I am of mature age and am a resident of New York City, New York.

During the spring of 1920 I was emplyed as assistant chemist at the laboratories of the States Metals Corporatibn at 131 Harris Avenue, Long Island City.

On or about April 8, 1920, I assisted Mr. Henry S. Doty in conducting tests to determine the relative merits of diphenylguanidine as an accelerator of rubber vulcanization as compared with hexamethylene-tetramine, using therefor a sample of diphenlyguaindine which said Doty provided for that purpose. Said tests comprised the introduction of equal quantities of both of said materials into different batches of so-called "tread stock" and vulcanizing the same for equal periods of time. The results of said tests showed that diphenylguanidine was much superior to hexamethyltetramine in point of time required

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for vulcanization and in the qualities of the vulcanized product.

I also assisted said Doty in similar tests conducted at said place during the first part of June, 1920, and the results of the same were to the same effect as the previous tests. I have examined "Exhibit A" attached to the affidavit of Henry S. Doty and state of my own knowledge that said exhibit represents the results of said tests of June, 1920.

Chester Frankenstein

Sworn to and subscribed before
me this 27th day of January,
1922.

Walter S. Davies.
Notary Public,
New York Co.

Sig.3.

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COPY

"EXHIBIT C."

J.A.KENDALL
524 Second National Bldg.,

SUBJECT:

AKRON, OHIO, Aug.26,1920.

Racine Auto Tire Co.,
Racine, Wisc.

Gentlemen:-

Attention Mr. A. H. Brehm.

We are pleased to announce the placing of a new ACCELERATOR "STATES X-L-O" upon the market. This ACCELERATOR is a noteworthy addition to the widely known compounding ingredients manufactured by FRAZAR & CO. New York.

"STATES X-L-O" has the unique qualities of -

POWERFUL TENSILE STRENGTH -
20% Higher Tensile with Same Elongation as the best now on the market.
QUICK CURE
Vulcanization effected in 3/4 TIME of any Accelerator now produced.
NON-POISONOUS PROPERTIES
There is NO ODOR WHATEVER in curing room nor in FINISHED COMPOUNDS.
NO RASH nor SKIN TROUBLE ANNOYS WORKMEN.
DURABILITY
Has superior power on compounds in DURABILITY AND AGEING.
LOWEST PRICE COMPATIBLE WITH QUALITY.
$2.50 per lb., f.o.b. Brooklyn, N.Y.
IMMEDIATE SHIPPING FACILITIES.
Quantity production assures PROMPT DELIVERIES. "X-L-O" packed in approx. 100 lb. paper lined wooden barrels.

There is an enormous embryonic demand already created for this Accelerator, and we believe prompt action on your part will be rewarded by immediate saving in dollars and time.

Are these strong features of vital interest to your compounding staff? We believe that you cannot afford to miss this opportunity to investigate a new Accelerator.

We thank you heartily for your attention.

Yours very truly,
J.A.KENDALL.

CHH:M
LCT

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COPY

EXHIBIT C (2)

.A.KENDALL
24 Second National Bldg.

SUBJECT:

AKRON, OHIO, Aug.26,1930

Brunswick-Balke-Collender Co.,
Muskegon, Mich.

Gentlemen:-

Attention Mr. A. Brill.

We are pleased to announce the placing of a new ACCELERATOR "STATES X-L-O" upon the market. This ACCELERATOR is a noteworthy addition to the widely known compounding ingredients manufactured by FRAZAR & CO., New York.

"STATES X-L-O" has the unique qualities of -

POWERFUL TENSILE STRENGTH
20% Higher Tensile with Same Elongation as the best now on the market.
QUICK CURE
Vulcanization effected in 3/4 TIME of any Accelerator now produced.
NON-POISONOUS PROPERTIES
There is NO ODOR WHATEVER in curing room nor in FINISHED COMPOUNDS.
NO RASH nor SKIN TROUBLE ANNOYS WORKMEN.
DURABILITY
Has superior power on compounds in DURABILITY AND AGEING.
LOWEST PRICE COMPATIBLE WITH QUALITY
$2.50 per lb., f.o.b. Brooklyn, N.Y.
IMMEDIATE SHIPPING FACILITIES
Quantity production assures PROMPT DELIVERIES. "X-L-O" packed in approx. 100 lb. paper lined wooden barrels.

There is an enormous embryonic demand already created for this Accelerator, and we believe prompt action on your part will be rewarded by immediate saving in dollars and time.

Are these strong features of vital interest to your compounding staff? We believe that you cannot afford to miss this opportunity to investigate a new Accelerator.

We thank you heartily for your attention.

Yours very truly,

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GHH:M
LCT

J.A.KENDALL

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COPY

EXHIBIT C

J.A.KENDALL
524 Second National Bldg.

SUBJECT:

AKRON, OHIO, Aug.26,192

The Mason Tire & Rubber Co.,
Kent, O.

Gentlemen:-

Attention Mr. C. D. Rockwood

We are pleased to announce the placing of a new ACCELERATOR "STATES X-L-O" upon the market. This ACCELERATOR is a noteworthy addition to the widely known compounding ingredients manufactured by FRAZAR & CO. New York.

"STATES X-L-O" has the unique qualities of -

POWERFUL TENSILE STRENGTH
20% Higher Tensile with Same Elongation as the best now on the market.
QUICK CURE
Vulcanization effected in 3/4 TIME of any Accelerator now produced.
NON-POISONOUS PROPERTIES
There is NO ODOR WHATEVER in curing room nor in FINISHED COMPOUNDS.
NO RASH nor SKIN TROUBLE ANNOYS WORKMEN.
DURABILITY
Has superior power on compounds in DURABILITY AND AGEING.
LOWEST PRICE COMPATIBLE WITH QUALITY
$2.50 per lb., f.o.b. Brooklyn,N.Y.
IMMEDIATE SHIPPING FACILITIES
Quantity production assures PROMPT DELIVERIES. "X-L-O" packed in approx. 100 lb. paper lined wooden barrels.

There is an enormous embryonic demand already created for this Accelerator, and we believe prompt action on your part will be rewarded by immediate saving in dollars and time.

Are these strong features of vital interest to your compounding staff? We believe that you cannot afford to miss this opportunity to investigate a new Accelerator.

We thank you heartily for your attention.

Yours very truly,

CHH:M
LCT

J.A.KENDALL.

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PURCHASE ORDER

NEW CASTLE RUBBER COMPANY

NEW CASTLE, PA.

J. A. Kendall,
524 -2d Nat'l. Ex. Bldg.,
Akron, Ohio.

IMPORTANT: ALL SHIPMENTS AND CORRESPONDENCE SHALL BE ADDRESSED TO OUR FACTORY
MANORINGTOWN, PA

THESE NUMBERS SHALL BE SHOWN ON ALL SHIPPING PAPERS, INVOICES AND RECEIPTED CORRESPONDENCE

ORDER NO. V4788

CLASSIFICATION: V L WE

REQUISITION NO. 9235

PLEASE ENTER OUR ORDER AS PER SPECIFICATIONS AND CONDITIONS HEREIN SET FORTH

DATE 8-302-0

ITEMS:	PRICE
1 lb. sample of "States X-L-O"	
Rush shipment.	
In accordance with your letter 8-26-20	
Kindly advise price by return mail.	
	M.S.& T. - SEP

NOTE: ALL INVOICES MUST BE RENDERED IN DUPLICATE AND ONLY WHEN ACCOMPANIED BY ORIGINAL EXPRESS RECEIPT OR BILL OF LADING

ACCEPTANCE AND IN CONSIDERATION HEREOF THE VENDOR WARRANTS THAT THE ABOVE ARTICLES DO NOT INFRINGE ON ANY UNITED STATES PATENT, THAT HE WILL DEFEND ANY SUIT THAT MAY ARISE IN RESPECT THERETO, AND THAT HE WILL SAVE THE VENDEE HARMLESS FROM ANY LOSS WHICH MAY BE INCURRED BY THE ASSERTION OF ANY PATENT RIGHTS THEREIN.
ORDER MUST NOT BE FILLED AT HIGHER PRICES THAN LAST QUOTED OR CHARGED WITHOUT ADVICE.
ALLOW NO CHARGE FOR BOXING, PACKING OR CARTING UNLESS BY AGREEMENT.
RESERVE THE RIGHT TO CANCEL THIS ORDER OR ANY UNFILLED PORTION THEREOF IF DELIVERIES ARE NOT MADE AS SPECIFIED HEREIN.
NO LOCAL CHECK TO BE ACCEPTED IN PAYMENT WITHOUT DISCOUNT FOR COLLECTING.
IN THE EVENT OF FIRE, FLOOD, STRIKES, LOCKOUT, ACCIDENT, WAR OR OTHER CAUSES BEYOND OUR CONTROL INTERFERING WITH THE PRODUCTION OR THE TRANSPORTATION OF THE GOODS HEREIN DESCRIBED, DELIVERIES UNDER THIS ORDER MAY BE SUSPENDED DURING THE PERIOD REQUIRED TO REMOVE THE CAUSE.

TERMS	F.O.B.	SHIP VIA.
2-10-30		Parcel post

NEW CASTLE RUBBER COMPANY

CAM: VK

Purchasing Agent

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SE IN CENTER

#6

IN THE UNITED STATES PATENT OFFICE.

In re Application of	:	Division 15; Room 308.
MORRIS L. WEISS,	:	
Serial No. 514,727;	:	VULCANIZATION ACCELERATORS.
filed November 12, 1921.	:	

New York, January 30, 1922.

HON. COMMISSIONER OF PATENTS,

Washington, D. C.

Sir:-

Attached hereto is an additional affidavit of Van Lear Woodward which it is desired to submit as supplementary to the affidavits of Morris L. Weiss, Henry S. Doty, and Chester Frankenstein forwarded with the letter to the Patent Office of January 27, 1922. This affidavit is sent at this time in view of the fact that said Van Lear Woodward was away from the City of New York during the latter part of last week and was not available to execute the affidavit at that time.

Trusting that the application will receive prompt action for the reasons stated, we are

Very respectfully,

MORRIS L. WEISS,

By Sheffield & Betts
his Attorneys.

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COPY

IN THE UNITED STATES PATENT OFFICE.

- - - - - - - - - - - - - - - -

In re Application of : Division 15; Room 308.

MORRIS L. WEISS, :

Serial No. 514,727; : VULCANIZATION ACCELERATORS

filed November 12, 1921. :

- - - - - - - - - - - - - - -:-

AFFIDAVIT OF VAN LEAR WOODWARD.

STATE OF NEW YORK)
: ss.:
COUNTY OF NEW YORK)

VAN LEAR WOODWARD, being duly sworn, deposes and says as follows:

I am Vice President of the Dovan Chemical Corporation, assignee of the above entitled application.

On or about April 7, 1920, Morris L. Weiss, the above mentioned applicant, called at my office, No. 30 Church Street, New York City, and explained to myself and Henry S. Doty the invention set forth in said application. At said time and place said Weiss delivered to said Doty and myself a sample of diphenylguanidine and explained to me and said Doty the manner and method of using the same as an accelerator in the vulcanization of rubber articles. Thereupon said Doty agreed to make tests of said sample in the valcanization of rubber and on or about April 8, 1920, said tests were conducted by said Doty at the laboratories of the States Metals Company, of Long Island City, New York. Immediately there-

after I was advised by said Doty that said tests had proved entirely satisfactory and the results obtained therefrom, using the same as an accelerator in the vulcanization of rubber, were superior to the results obtained when using hexamethylene tetramine. In view of the results of said tests said Weiss, Doty and the deponent agreed to co-operate in the manufacture for the sale of diphenylguanidine as an accelerator. preparations were then made for the manufacture of the same in commercial quantities, and during the month of June, 1920, sufficient quantities of chemicals were purchased by said Weiss, Doty and the deponent to start the manufacture of said accelerator. I have examined the invoices attached to the affidavit of said Doty and marked "Exhibit B", and know them to be invoices for chemicals purchased as aforesaid.

About the middle of June, 1920, the deponent was shown the results of a series of tests made at the laboratories of said States Metals Company at Long Island City by said Doty using diphenylguanidine as an accelerator. I have examined "Exhibit A" attached to the affidavit of said Doty, and recognize the same as being a true report of said tests as I saw the same in June, 1920. Thereafter, from June 1920 to September 1920, about 150 pounds of diphenylguanidine were manufactured by at laboratories equipped for that purpose at 980 East 35th Street, Brooklyn, New York. I have examined copies of the letters attached to the affidavit of said Doty as "Exhibit C", and recognize the same as being true copies

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of letters sent out to various concerns manufacturing rubber goods advising them of the availability of diphenylguanidine as an accelerator for rubber vulcanization during the latter part of August, 1920, by our Akron agent or representative, J. A. Kendall. In "Exhibit C" references to "XLO" refer to the accelerator comprising diphenylguanidine as the active agent thereof. Beginning about the last week in August 1920 samples of the same were sent to various manufacturers of rubber goods, including the General Tire & Rubber Company, of Akron, Ohio, and the Goodyear Tire & Rubber Company, of Akron, Ohio, and others.

The sales of said accelerators were begun during September, 1920, and were made to various rubber manufacturing concerns, including the Dunlop Tire & Rubber Company of America, of Buffalo, New York, the Mason Tire & Rubber Company, of Kent, Ohio, the New Castle Rubber Company, of New Castle, Penna., and others.

I recognize "Exhibit D" attached to the affidavit of said Doty as an order for diphenylguanidine as an accelerator sent to us through said J. A. Kendall and received at our office on September 2, 1920.

I have read the affidavits of said M. L. Weiss and said Henry S. Doty and would state that the same are true in all respects to the best of my knowledge, information and belief.

Van Lear Woodward

Sworn to and subscribed before me this 30 day of January, 1922.

Edna L. Krieger

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M/MSY

ADDRESS ONLY THE COMMISSIONER OF PATENTS, WASHINGTON, D. C.

Div. 15 S-181 **Serial No.** 514,727

DEPARTMENT OF THE INTERIOR

UNITED STATES PATENT OFFICE

WASHINGTON Feb. fifteen, 1922

Morris L Weiss, Assor. etc.

Sir: Your APPLICATION for a patent for an IMPROVEMENT in Vulcanization Accelerators

filed Nov. 12, 1921, has been examined and ALLOWED. (12 claims)

The final fee, TWENTY DOLLARS, must be paid not later than SIX MONTHS from the date of this present notice of allowance. If the final fee be not paid within that period, the patent on this application will be withheld, unless renewed with an additional fee of $15, under the provisions of Section 4897, Revised Statutes.

The office delivers patents upon the day of their date, and on which their term begins to run. The printing, phbtolithographing, and engrossing of the several patent parts, preparatory to final signing and sealing, will require about four weeks, and such work will not be undertaken until after payment of the necessary fee.

When you send the final fee you will also send, DISTINCTLY AND PLAINLY WRITTEN, the name of the INVENTOR, TITLE OF INVENTION, AND SERIAL NUMBER AS ABOVE GIVEN, DATE OF ALLOWANCE (which is the date of this circular), DATE OF FILING, and, if assigned, the NAMES OF THE ASSIGNEES.

If you desire to have the patent issue to ASSIGNEES, an assignment containing a REQUEST to that effect, together with the FEE for recording the same, must be filed in this office on or before the date of payment of final fee.

After issue of the patent uncertified copies of the drawings and specifications may be purchased at the price of TEN CENTS EACH. The money should accompany the order. Postage stamps will not be received.

Final fees will NOT be received from other than the applicant, his assignee or attorney, or a party in interest as shown by the records of the Patent Office.

Respectfully,

Thomas E. Robertson

Commissioner of Patents.

IN REMITTING THE FINAL FEE GIVE THE SERIAL NUMBER AT THE HEAD OF THIS NOTICE.

UNCERTIFIED CHECKS WILL NOT BE ACCEPTED.

Sheffield and Betts

52 William St.

New York, N.Y.

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20 /

1922 FEB 9 U.S.PAT.OFFICE

2—337.

MEMORANDUM
OF
FEE PAID AT UNITED STATES PATENT OFFICE.

(Be careful to give correct Serial No.)

Serial No. 514727, 19..

INVENTOR:
Morris L. Weiss

PATENT TO BE ISSUED TO
As per record.

NAME OF INVENTION, AS ALLOWED:
Valve mechanism Accelerator

DATE OF PAYMENT:
Feb. 17, 1922

FEE:
$20 Twenty

DATE OF FILING:
November 12, 1921

DATE OF CIRCULAR OF ALLOWANCE:
Feb. 15-1922

The Commissioner of Patents will please apply the accompanying fee as indicated above, on
[illegible] in the issue of March 7, 1922.

REMIT $ 20.00

Sheffield & Betts
Attorney.

[illegible] Div. B.
Feb. 20, 1922.

SEND PATENT TO
Sheffield & Betts
52 William St
New York, N.Y.

9—3885

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ADDRESS ONLY THE COMMISSIONER OF PATENTS, WASHINGTON, D. C.

2—74

DEPARTMENT OF THE INTERIOR.
UNITED STATES PATENT OFFICE.

Washington, D. C., Feb. 20, 1922, *192*

MORRIS L. WEISS, Assor.

Sir:

Your application for patent for an improvement in

Vulcanisation 'ccelerators,

*serial No.*514,727 *, allowed* Feb. 15, 1922

has been WITHDRAWN from the ISSUE FILES in this office. The reasons therefor will be communicated to you by the Examiner.

THE FINAL FEE WILL BE REFUNDED IN DUE COURSE OF BUSINESS.

Until a new notice of allowance is sent you the final fee will not be required.

Very respectfully,

T.E.Robertson

Commissioner of Patents.

Shaffield and Batts,
52 William Street,
New York,N.Y.

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5 Room 308 2-220 Paper No. 7

Address only "The Commissioner of Patents, Washington, D.C." and not any official by name.

All communications respecting this application should give the serial number, date of filing, title of invention, and name of the applicant.

DEPARTMENT OF THE INTERIOR
UNITED STATES PATENT OFFICE

WASHINGTON Feb. 23,1922

Sheffield & Betts

52 William st.

New York, N.Y.

Please find below a communication from the EXAMINER in charge of the application of

M.L.Weiss,Ser.No.514,727,filed Nov. 12,1921; Vulcanization Accelerators.

Thomas E. Robertson
Commissioner of Patents

This application allowed Feb.15,1922 has been withdrawn from issue . Feb.20,1922 for the reason that the following new reference may be applied to the claim : Journal of Industrial and Engineering Chemistry Vol.XII No.4 page 317,— 322 filed in U.S.Patent Office April 5 1920 Published by the American Chemical Society. The claims are rejected on said publication on page 322 Experimental Part - a method is stated for testing accelerator- on some Page Table I discloses Diphenylguanidine as one of those tested. On page 319 first paragraph - line 6 the conclusions of the authers are stated as to diphenylguanidine.

Applicant discloseses of the use of said accelerator are not more specific than disclosed in the publication, hence the rejection in as much as applicants affidavit under Rule 75 shows no completion of the invention prior to Apr. 5,1920 but merely conception.

M.L. Rearson
Examiner.

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ADDRESS ONLY THE COMMISSIONER OF PATENTS WASHINGTON, D. C.

Letters No.

DEPARTMENT OF THE INTERIOR

UNITED STATES PATENT OFFICE

WASHINGTON Feb. 20,1922

Hon. Commissioner of Patents

It is respectfully requested that application of Morris L Weiss Ser. No.514,727 filed Nov. 12,1921 allowed Feb.14,1922 be withdrawn from issue (final fees having been paid) for the purpose of rejecting the claims on a newly discovered reference- a publication "Journal of Industrial and Engineering Chemistry Vol XII No.4. page 317 -322. This publication was filed in the Office on April 5, 1920 - as evidenced by the library stamp on page 313 of the above volume.

In a prior rejection on another publication applicant under Rule 75 overcame the date Sept. 6,1920 and states that he conceived the invention prior to Jan. 1,1920. (affidavit of applicant Morris L Weiss filed Jan. 28,1922 paper No.5 and further states that on April 7,1920 he disclosed the invention to others and that it was tried and reduced to practice about April 8,1920. The reference on which the Examiner now desires to reject the claims was as stated above filed in the Office on April 5,1920. This reference is a publication by the American chemical Society of an address alleged to have been presented before the Rubber section at the 58th meeting of the American Chemical Society., Phila, Pa Sept. 2 - 6 1919 . Said publication

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alleges that the substance Diphenylguanidine had been tested as an accelerator page 319 line 23-25 and on Page 322 it mentions Diphenylguandine Table 1, as one of the substances that had been tested in the preliminary experiments which the authors of the article conducted. But it is stated on same page 322 after Table II -.

"As these preliminary test were conducted solely for guidance in subsequent experiments. we do not feel warranted in drawing extensive conclusions from them"

The publication is a clear disclosure of the use of di and And triphenylguanidine as an accelerator broadly, and as applicant's specification is no more than a broad disclosure of the use of the same reagent without disclosing any details other than that usually employed with accelerators of this class, it is considered that the publication constitutes a reference for the claims.

Carl Thuring

Respectfully

M. L. Redron,

Examiner, Div. 15.

Feb. 20/22

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JAMES R. SHEFFIELD
L. P. H. BETTS
JOHN W. PETERS
JAMES J. CORGROVE
EDWARD W. VAILL
ABEL E. BLACKMAR, JR.

SHEFFIELD & BETTS
COUNSELLORS AT LAW
52 WILLIAM STREET
NEW YORK

SAMUEL R. BETTS
COUNSEL

February 23, 1922

Hon. Commissioner of Patents
Washington, D. C.

Re Application of Morris L. Weiss
Serial No. 514,727
Filed November 12, 1921.
Allowed February 15, 1922.
Withdrawn from Issue Feb. 20, 1922.

Attention of the Financial Clerk

Dear Sir:

We are in receipt of the notice dated February 20, 1922, advising us of the withdrawal of the above mentioned application from the issue files of the Patent Office. We also note that "the final fee will be refunded in due course of business".

In view of the expected early reallowance of this application, we desire to request that this final fee be held subject to our order and instructions in connection with the reallowance of this application. It may be possible that we shall desire to telegraph you to apply this final fee to the same application immediately upon reallowance, which we trust can be done by telegram.

Yours respectfully,

Sheffield & Betts

SWV/K

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(889)

SHEFFIELD & BETTS
COUNSELLORS AT LAW
52 WILLIAM STREET
NEW YORK

SAMUEL R. BETTS
COUNSEL

February 24, 1922

#9½

Hon. Commissioner of Patents
Washington, D. C.

Attention of Chief of Issue Division

Re Application of M. L. Weiss, Ser. #514,727
Filed Nov.12,1921,-Vulcanization Accelerators

S i r :

Please advise Messrs. Milans & Milans of #908 G St., N. W,, Washington, immediately upon the reallowance of the above entitled application.

Sheffield & Betts.
Attorneys for M. L. Weiss

EWV/K

IN THE UNITED STATES PATENT OFFICE

In re Application of	
MORRIS L. WEISS	
Serial No. 514,727	Div. 15 - Room 308
Filed November 12, 1921	
VULCANIZATION ACCELERATORS	

New York, February 24, 1922

HONORABLE COMMISSIONER OF PATENTS

Washington, D. C.

S i r :

In response to the official action of February 23, 1922, resulting from the withdrawal of the above entitled case from the Issue Division on February 20, 1922, the accompanying affidavits of Morris L. Weiss, Monroe H. Daniels, Harvey W. Seil, Isidor Greenwald and Reuben Schulich, are submitted under Rule 75 in order to overcome the publication in the Journal of Industrial and Engineering Chemistry, page 317, vol. 12, of 1920.

These affidavits also antedate September 2, 1919, the date alleged in the publication as being that upon which the authors read papers at the Philadelphia meeting of the American Chemical Society.

This inventor is undoubtedly the pioneer in the art relative to the substance claimed in this specification as an accelerator and evidence of earlier dates still than those now alleged might be obtained but earlier dates

are thought not to be necessary at this time since only sufficient evidence to overcome the references cited by the Patent Office is now required. In view of the unexpected delay which has been caused in this case by the discovery of the publication last cited, it is requested that the application be taken up for action immediately and passed to issue at the earliest possible moment.

Very respectfully,

MORRIS L. WEISS

by his Attorneys

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IN THE UNITED STATES PATENT OFFICE

- - - - - - - - - - - - - -

In re Application of :

MORRIS L. WEISS, :

Serial No.514,727 : Div. 15 - Room 308

Filed Nov. 12, 1921 :

VULCANIZATION ACCELER- :

ATORS. :

- - - - - - - - - - - - - -

STATE OF NEW YORK,)
: ss.:
COUNTY OF NEW YORK)

MORRIS L. WEISS, being duly sworn, depeses and says as follows:

I am the Morris L. Weiss named in the above entitled application.

During the year 1919 I was employed by the Republic Rubber Company located at Youngstown, Ohio, as research chemist under Monroe H. Daniels, who was chief chemist for said Company. Prior to January 1, 1919, I conceived the possibilities of using diphenylguanidine as an accelerator in the vulcanization of rubber compounds and after disclosing the same to said Daniels I proceeded with the production and test of said diphenylguanidine as accelerator. Said accelerator was produced and actually used in the vulcanization of rubber goods during the early part of the year 1919. During the month of March, 1919, at a meeting of the Youngstown Chemical Society, I had a

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conversation with Harvey A. Neil and disclosed to him my invention, including the fact of my previous production and use of diphenylguanidine as an accelerator for vulcanizing rubber compounds.

During the Spring of the year 1919 I wrote to Dr. Isidor Greenwald, my former chief chemist at the Harriman Research Laboratory of New York, who was then a Lieutenant in the Sanitary Corps U. S. Army, located at Camp Mead, Maryland, and advised him that I had produced and used diphenylguanidine as an accelerator for rubber vulcanization and that if he so desired I would send him a sample for use in his research work. He replied that owing to his duties at that time he was unable to use the material.

During the last week of March, 1920, I went to New York and prior to the first of April, 1920, I called at the office of Messrs. Doty & Woodward, and thereafter during the first week of April, 1920, delivered to them a sample of diphenylguanidine as set forth in my prior affidavit executed January 27, 1922.

Morris L. Weiss

Subscribed and sworn to before
me this 24th day of February, 1922.

Walter S. Jones
Notary Public,
New York County.

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IN THE UNITED STATES PATENT OFFICE

In re Application of

MORRIS L. WEISS

Serial No. 514,727 Div. 15 - Room 300

Filed November 12, 1921

VULCANIZATION ACCELERATORS

New York, February 1922

STATE OF NEW YORK)
(SS:
COUNTY OF NEW YORK)

HARVEY A. SEIL, being duly sworn, deposes and says as follows:

I am of mature age and a resident of Rutherford, New Jersey; I am a chemist by profession and conduct a chemical Laboratory at 128 Water Street, New York City, N. Y.

During the year 1919, I was chief chemist for the Youngstown Chemical Company at Youngstown, Ohio. Prior to the month of April, 1919, I met Morris L. Weiss at a meeting of the Chemical Society in Youngstown, Ohio, at which meeting I read a paper. I then and there had a talk with said Weiss about accelerators for rubber compounds, during which said Weiss told me that he had been working on the production of diphenylguanidine as an accelerator for vulcanizing rubber compounds and that said substance had proved to be very efficient for that purpose.

Harvey A. Seil.

Sworn to and subscribed before
me this 23 day of February, 1922.

Walter S. Jones Notary Public
New York Co

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IN THE UNITED STATES PATENT OFFICE

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In re Application of :

MORRIS L. WEISS, : Division 15; Room 306.

Serial No. 514,727; :

filed Nov. 12, 1921; :

VULCANIZATION ACCELERATORS :

- - - - - - - - - - - - - -

STATE OF NEW YORK)
: ss.:
COUNTY OF NEW YORK)

ISIDOR GREENWALD, being duly sworn, deposes and says as follows:

I am of mature age and a research chemist employed at the Harriman Research Laboratory, 59th Street and Ninth Avenue, Borough of Manhattan, City, County and State of New York.

Mr. Morris L. Weiss has been known to me for about ten years and for four years acted as my assistant. He became acquainted with some of the work I was doing and in which I did some work with methylguanidine. His association with my work ended about the year 1916.

I was in the U. S. Army from December 1917 to May 1919. From October 26, 1918, to May 6, 1919, I was stationed at Camp Mead, Maryland, as Lieutenant, Sanitary Corps. During my duty at this Camp I received a letter from Morris L. Weiss at Youngstown, Ohio, offering me a sample of diphenylguanidine for experimental work, he having stated that said substance had been produced

by him for use in the acceleration of the vulcanization of rubber compounds. Not being able at that time to continue my researches, nor being specifically interested in that class of guanidines, I wrote to him declining his offer.

Sidon Greenwald

Sworn to before me this
24th day of Febuayy,
1922.

Walter S. Jones
Notary Public,
New York Co.

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IN THE UNITED STATES PATENT OFFICE

In re Application of

MORRIS L. WEISS

Serial No. 514,727 — Div. 15 - Room 308

Filed November 12, 1921

VULCANIZATION ACCELERATORS

New York, February 2nd 1922.

STATE OF NEW YORK)
(SS:
COUNTY OF NEW YORK)

REUBEN SCHULICH, being duly sworn, deposes and says as follows:

I am of mature age and a resident of the Borough of Bronx, City, County and State of New York; during the years 1919 and 1920, I resided at Youngstown, Ohio, prior to which time I had become acquainted with Morris L. Weiss, whom I knew as a rubber chemist. About the middle of March, 1920, I called at the residence of Morris L. Weiss, at Youngstown, Ohio, and then and there discussed with him accelerators for rubber vulcanization and which discussion related to guanidines, including diphenylguanidine , which latter, said Weiss told me, he had previously produced and used as an accelerator for the vulcanization of rubber goods. The month of March is fixed in the mind of deponent by reason of the fact that during the month of January, 1920, deponent was ill with an attack of

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influenza and subsequent to March 1, 1920, for several weeks, was not regularly employed as a chemist. During this period of unemployment deponent visited the residence of Morris L. Weiss and the conversation above referred to took place.

Reuben Schulick.

Sworn to before me this
23rd day of February, 1922.

Walter S. Jones.
Notary Public
New York Co.

IN THE UNITED STATES PATENT OFFICE.

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In re Application of :

MORRIS L. WEISS, : Division 15; Room 308.

Serial No. 514,727; :

filed Nov. 12, 1921; :

VULCANIZATION ACCELERATORS. :

- - - - - - - - - - - - -

STATE OF PENNSYLVANIA, :

: ss.:

County of :

MONROE H. DANIELS, being duly sworn, deposes and says as follows:

I am of mature age and reside at Youngstown, Ohio.

During the year 1919 I was chief chemist of the Republic Rubber Company at Youngstown, Ohio. During that year Morris L. Weiss was employed as research chemist in my department in connection with the development of accelerators for rubber compounds. During the early part of the year 1919 said Weiss produced diphenylguanidine as an accelerator for rubber compounds, and during the early part of that year made numerour tests of the same as an accelerator in vulcanizing rubber. These tests were also carried out in the compounding laboratory for the various departments of the Republic Rubber Company at Youngstown, Ohio, and the accelerator proved to

be highly efficient as an accelerator in the actual vulcanization of rubber goods, such as hose, tires, belts, valves and other mechanical goods.

Thomas A. Davies

Sworn to and subscribed
before me this 25th day
of February, 1922.

Fay C. Miller
Notary Public,
County.

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February 28, 1922. #10

Messrs. Sheffield & Betts,
52 William Street,
New York,N. Y.

Gentlemen:

Referring to your communication of the 23rd inst., relative to withholding the final fee in the application of Morris L. Weiss, Serial No. 514,727, you are advised that your request will be granted.

Respectfully,

Wm. I. Wyman,
Chief Clerk.

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8.

B—272.

MEMORANDUM

OF

FEE PAID AT UNITED STATES PATENT OFFICE.

(Be careful to give correct Serial No.)

Serial No. 514727, 19...

INVENTOR:

Morris L. Weiss

PATENT TO BE ISSUED TO

as per record

NAME OF INVENTION, AS ALLOWED:

Vulcanization Accelerator

DATE OF PAYMENT:

March 1-1922

FEE:

$20- Twenty

DATE OF FILING:

November 12-1921

DATE OF CIRCULAR OF ALLOWANCE:

March 1-1922

The Commissioner of Patents will please apply the accompanying fee as indicated above.

REMIT $20.00

P.M.M.

Chief Issue Div.

Sheffield & Betts

Attorney.

March 18,19222

SEND PATENT TO

Sheffield & Betts

52- William St.

New York, N.Y.

B—1788

Duplicate fee

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ADDRESS ONLY THE COMMISSIONER OF PAT. WASHINGTON, D. C.

H/MWY
Div.15 2-182

DEPARTMENT OF THE INTERIOR
UNITED STATES PATENT OFFICE
WASHINGTON

Serial No.
514,727

Mar. one, 1922

Morris L Weiss, Assor. etc.
c/o Sheffield and Betts
52 William St.
New York, N.Y.

Sir:

Your APPLICATION for a patent for an IMPROVEMENT

Vulcanization Accelerators

filed Nov. 12, , 1921, has been examined and ALLOWED. (12 clms)

The final fee, TWENTY DOLLARS, having been received, the Letters Patent will be forwarded in due course of business.

Additional copies of specifications and drawings will be charged for at the following rates: Single copies, uncertified 10 CENTS EACH. The money should accompany the order.

Respectfully,

Wm. D. Hyman

Chief Clerk.

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SHEFFIELD & BETTS
COUNSELLORS AT LAW
52 WILLIAM STREET
New York

SAMUEL R. BETTS
COUNSEL

March 3, 1922

B

Hon, Commissioner of Patents
Washington, D. C.

Attention of William I. Wyman
Re Application of Morris L. Weiss,
Serial No. 514,727

S i r :

Replying to your favor of the 28th ult., just received, we would say that the final fee on this application has been paid by the deposit of another $20. in view of the fact that we did not receive the reply to our letter of the 23rd in time. We will, therefore, have to ask you to kindly refund the previous fee referred to in your letter of the 28th ult.

Yours very truly,

Sheffield & Betts.

SWV/K

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March 18, 1922.

Messrs. Sheffield and Betts,
52 William Street,
New York, N. Y.

Gentlemen:

Referring to your communication of recent date transmitting the final fee of $20.00 in the application of Morris L. Weiss, exor. Serial No. 514,727, you are advised that this fee is a DUPLICATE FINAL FEE and will be refunded in due course of business.

Letters Patent will be granted March 28, 1922 and will be forwarded to you at the above address.

Respectfully,

Wm. I. Wyman,
Chief Clerk.

Sig. 5.

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United States District Court

Southern DISTRICT OF New York

HONORABLE COMMISSIONER OF PATENTS,
Washington, D. C.

SIR:

In compliance with the Act of February 18, 1922 (41 Stat. L. ....), you are advised that there was filed on the 29 day of May, 1922, in this court an action, suit, or proceeding No. E-24-23, entitled:

Name Donovan Chemical Corporation, Plaintiff,
Address Brooklyn, NY

versus

Name National Aniline & Chemical Company, Inc., Defendant,
Address New York City

brought upon the following patents:

	PATENT NO.	DATE OF PATENT	PATENTEE
1	1 411 231	March 28 1922	Morris L. Haas
2			
3			
4			
5			

In the above-entitled case, on the ..... day of ....., 192 the following patents have been included by ..... (insert amendment, answer, cross bill, or other pleading):

	PATENT NO.	DATE OF PATENT	PATENTEE
1			
2	Def. No. 12		
3			
4			
5			

In the above-entitled case the following decision has been rendered or decree issued:

In witness whereof I have affixed my hand this 24th day of November, 1922, at New York NY

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Clerk of said Court.

United States District Court

Southern DISTRICT OF New York

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HONORABLE COMMISSIONER OF PATENTS,
Washington, D. C.

SIR:

In compliance with the Act of February 18, 1922 (41 Stat. L. ....), you are advised that there was filed on the 29th day of May, 1922, in this court an action, suit, or proceeding No. E-11-23, entitled:

Name Doran Chemical Corporation, Plaintiff,
Address State of Delaware

Name National Oildraw Chemical Company Inc. Defendant,
Address Jersey City, N.J.

brought upon the following patents:

PATENT NO.	DATE OF PATENT	PATENTEE
1. 1411231	March 28 1922	Doran Chemical Corporation
2.		
3.		
4.		
5.		

In the above-entitled case, on the ..... day of ....., 192 the following patents have been included by ..... (insert amendment, answer, cross bill, or other pleading):

PATENT NO.	DATE OF PATENT	PATENTEE
1.		
2. See No. 11		
3.		
4.		
5.		

In the above-entitled case the following decision has been rendered or decree issued:

By Manton, Judge, interlocutory decree sustaining said patent, adjudging that defendants had infringed upon said patent, and granting perpetual injunction restraining defendant. Filed Feb. 21 1923.

In witness whereof I have affixed my hand this 23d day of April, 1923, at New York, N.Y.

Clerk.

By Manton, Judge, order suspending injunction pending appeal to the Circuit Court of Appeals. Filed Feb 23 1923

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1921

CONTENTS:

1. Application ____ papers.
2. Re: Dec 29, 1921
3. Catch & Affs. Jan 6, 1922
4. Pet Jan 13, 1922
5. Affs & Print Jan 28, 1922
6. Affs Jan 31, 1922
7. Letter Feb 20, 1922
8. Letter of Withdrawal Issue, Febr 24, 1922
9. Letter Feb 24 1922
10. Letter (C) Feb 25, 1922
11. Notice of Suit, Nov. 28-29
12. Decree of Suit, April 4-23
13. ____
14. ____
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ter is removed. The crucible and contents are dried and weighed. The next step is acetylation with acetic anhydride, after which the cellulose acetate is removed by washing with acetone. Cellulose is determined by difference.

The Variability of Crude Rubber, JOHN B. TUTTLE.—This paper consisted chiefly of a résumé of previous work by Eaton and Granthan, de Vries and others. This is a subject on which not a great deal of work has been done in this country.

The Action of Accelerators During Vulcanization, J. H. SCOTT.—Detailed experiments by Spence and the author were described. These consisted of the introduction as dry powder of various alkaline substances, such as NaOH, Na_2CO_3, $Ba(OH)_2$, soda lime and MgO; dipping in alkaline solutions; and the washing of rubber with caustic.

Considerable reduction in the period of vulcanization was shown by all alkalis tried. Zinc oxide was found to be an aid, while barytes was without effect. In addition the physical properties of the stocks were improved. Washing with alkali gave slightly improved physical properties but no decrease in time of vulcanization. Immersion in 5 per cent NaOH solution for 24 hr. produced a slightly shorter cure with a little higher tensile strength.

The author pointed out that alkalis are not satisfactory accelerators, due probably to the bad aging properties of the compounds. The fact that they are accelerators is of considerable theoretical interest. They probably function by the hydrolysis of the nitrogenous matter of crude rubber to amino acids, which are powerful accelerators, comparing favorably with piperidine.

Mr. Scott defined the ideal accelerator as one capable of bringing about vulcanization in the shortest possible time consistent with factory practice and which produces maximum polymerization. It should also be nonpoisonous and easily handled. For some time it has been recognized by rubber chemists that accelerators have another effect than merely decreasing time of cure. The increase in tensile strength, snap, feel and nerve the author attributes largely to polymerization.

The Action of Certain Organic Accelerators in the Vulcanization of Rubber, C. D. KRATZ, A. H. FLOWER and COLE COOLIDGE.—This paper consisted of a review of experiments with aniline, urea, thiourea, mono-, di- and tri-phenyl thiourea and mono-, di- and tri-phenyl guanidine, anhydro formaldehyde aniline and paraphenylene diamine. The authors attribute the curing power of these accelerators to their decomposition at the temperature of vulcanization in the presence of sulphur-giving aniline, which they claim has a grouping which readily functions as a sulphur carrier. They recommend comparing accelerators in molecular quantities.

Reactions of Accelerators During Vulcanization, C. W. BEDFORD and WINFIELD SCOTT.—This paper is a reply to and a criticism of a recent paper by Dubosc in the *India Rubber World*. The authors stated that hexamethylene tetramine decomposes when heated with sulphur at the curing temperature and gives off CS_2, NH_3 and H_2S, but no acetylene, as claimed by Dubosc. They also stated that methylene aniline decomposes when heated under similar conditions, giving CS_2, aniline and thiocarbanilide.

The Effect of Organic Accelerators on the Vulcanization Coefficient, D. F. CRANOR.—The author gave in detail the results of experiments with hexamethylene-tetramine and the addition product similar to thiocarbanilide produced by the action of CS_2 on dimethylamine. He showed that the coefficient of vulcanization bears no direct relation to the physical properties. He obtained a technical cure with the dimethylamine addition product when the coefficient of vulcanization was aproximately 1.00. This falls in line with Scott's statement regarding the polymerizing influence of accelerators. Dimethylamine-dimethyl-dithiocarbamate is an extremely powerful accelerator. One-half per cent brings about a cure in 5 min. at 40 lb. steam.

Some Methods of Testing the Hardness of Vulcanized Rubber, H. P. GURNEY.—This paper consisted of a review of the different methods of determining hardness of rubber goods and contained data on the Shore hardometer and the Pusey-Jones plastometer.

The Manufacture and Use of Crimson Antimony, J. M. BIEBER.—The author gave a detailed description of the preparation of crimson antimony, i.e., antimony oxysulphide. The important points on the preparation are purely of antimony trichloride solution, and the concentration of the acid used for precipitation.

Research on Zinc Products for the Rubber Industry, P. R. CROLL and I. R. RUBY.—It was pointed out that the New Jersey Zinc Co. is very desirous of improving the quality of its zinc oxide for the rubber industry and has installed a rubber division in its new research laboratory for this purpose. Lantern slides showing the ultimate particles of zinc oxide were exhibited. Zinc oxide is crystalline and the particles vary in size from 0.1 to 1 micron, the average being 0.5 micron. Their microscopic work is excellent and is fundamental to an understanding of compounding phenomena.

Carbon Black—Its Properties and Uses, ST. J. PERROTT.—This paper was delivered in the Division of Industrial Chemists and Chemical Engineers and proved so interesting that Chairman Tuttle invited Mr. Perrott to give it also before the rubber division. The manner of producing gas black by incomplete combustion of natural gas, allowing the smoky flame to strike a cold metal surface (air cooled) was illustrated by lantern slides. From the black cloud issuing above the plant shown, one would gather that technique of this industry is not very highly developed. Mr. Perrott showed several slides of micro-photographs of gas black and stated that the particles varied in size from 30 to 100 milli-microns.

The paper of H. E. SIMMONS on the value of a library to the rubber laboratory was not given, but will be published soon. Owing to the absence of GEORGE OENSLAGER his paper on the testing of pigments was held over until the next meeting of the Rubber Division. The paper of C. OLIN NORTH on the effect of compounding ingredients on the physical properties of rubber was unfortunately not in final shape for presentation, but will doubtless be given at the next meeting of the division.

ELECTION OF OFFICERS

The officers elected for the coming year are Dr. WARREN K. LEWIS, chairman; and ARNOLD H. SMITH, secretary. Dr. Lewis is a well known member of the chemical engineering staff of Massachusetts Institute

Defendant's Exhibit K 212

Rubber Vulcanization Accelerators

BY ANDREW H. KING

This is a subject now attracting considerable attention in the rubber business. The possibilities seem almost unlimited. For example, a factory which has been using the old, well-known mineral accelerators can materially increase its capacity by the use of some one or more of the new organic catalysers, such as piperidine or para-phenylenediamine.

It is common knowledge that the degree of vulcanization can be greatly influenced by a change in either time or temperature. Thus a stock which cures ordinarily in 40 minutes at 40 lb. steam pressure can be vulcanized in 25 minutes at 60 lb. This is one way to speed up production. However, the increase in working steam pressure is expensive, and sometimes quite unsatisfactory. It is far better to add from 1 to 2 per cent of some good accelerator, and properly cure the rubber at low pressure, than to run chances of injuring the nerve by high temperature. In certain instances both high temperatures and accelerators are used, as in the case of cheap molded goods, where a large production is necessary to take care of the overhead.

An accelerator is merely a catalyser. It tends to increase the velocity of the reaction between sulfur and rubber during vulcanization. For the sake of clearness, I will enumerate a few conclusions deduced from numerous observations of the catalytic effect, sometimes called "the laws of catalysis":

1. The catalyser has the same chemical composition at the end of the reaction as it had in the beginning. This statement applies to nearly all accelerators, except certain of the organic compounds which are decomposed to a more or less extent at the temperature of vulcanization.

2. A catalytic agent is incapable of starting a reaction. It can only modify the velocity.

3. Very small quantities are sufficient to transform relatively large amounts of reacting substances.

4. The final state of equilibrium is independent of the nature and quantity of a catalyst.

5. Catalysers are of two kinds—positive and negative; i.e., they may either increase or retard the reaction velocity.

The above statements are based on observed facts. Just why they are so, and what the underlying principle of catalysis is, the future may explain. There are numerous theories which seem to fit separate cases quite well. Thus, the theory of surface concentration seems an excellent explanation of the behavior of platinum sponge in the contact process for sulfuric acid.

But the separate group of vulcanization accelerators seem to belong to the intermediate product family. It is thought that the catalyser unites with one of the reacting substances, forming an unstable compound, which in turn reacts with the other substance. In the course of this reaction, the catalyser is set free, and the process begins all over again.

An example of this phenomenon, though not a catalytic action in the true sense, is found in the commercial method for the preparation of aniline. Nitrobenzole is reduced by means of iron filings and hydrochloric acid. Only about one-fortieth of the theoretical quantity of acid is necessary. This is probably because iron filings and water are able to effect the reduction in the presence of ferrous chloride. In this instance it may be called a pseudo-catalyser. The reactions taking place are sometimes written as follows:

(1) $C_6H_5NO_2 + 3Fe + 6HCl \rightleftarrows 3FeCl_2 + 2H_2O + C_6H_5NH_2$

(2) $FeCl_2 + 2C_6H_5NH_2 + 2H_2O \rightleftarrows Fe(OH)_2 + 2C_6H_5NH_2.HCl$

(3) $2C_6H_5NH_2.HCl + Fe \rightleftarrows FeCl_2 + H_2 + 2C_6H_5NH_2$

(4) $C_6H_5NO_2 + 3H_2 \rightleftarrows C_6H_5NH_2 + 2H_2O$.

The halogen carriers, which are so important in organic preparations, are also pseudo-catalysers.

The chemical reaction between sulfur and rubber may be written:

Sulfur + Rubber ⇄ Polyprene Sulfide.

The speed of this reaction is influenced in proportion to the quantity of accelerator used, up to a certain limit, beyond which it acts as a retarder; that is, as a negative catalyser. As a general rule, accelerators should be used in small amounts, so as not to affect the nerve or quality of the rubber.

A peculiar fact has been noted. By a combination of accelerators the resulting increase in speed is greater than the sum of their individual increases, when acting alone. For example, the effect of 1 per cent tetramethylenediamine and 1 per cent piperidine exceeds the sum of the effects of the same catalysers when mixed in separate batches.

MINERAL ACCELERATORS

The chief mineral accelerators are:

Lime
Magnesia
Litharge
White lead
Zinc oxide

They are named in the order of their relative power.

Lime: The lime in common use is prepared by burning limestone and slacking the product by means of steam. Properly prepared, it is just a little short of complete hydration. In curing soft rubber from ½ to 2½ per cent may be used. For hard rubber larger amounts are customary.

Magnesia: The best magnesia is a heavy calcined product known as "Magnesia Usta." It is prepared by precipitating magnesium from solution in the form of magnesium carbonate and calcining the product. Magnesia finds a larger use than lime, though its curing action is only about half as great. Its advantage is that it leaves the nerve of the rubber absolutely unaffected, while lime has a slight hardening action. Combined with litharge it produces very satisfactory results.

Litharge and other lead compounds: Besides litharge, such compounds as white lead, sublimed white lead, and red lead are also valuable. Their use is limited, however, to black goods, and to those having high specific gravities. Stevens (*J. Soc. Chem. Ind.*, 34, 524-6, 1915) is of the opinion that the catalytic effect of litharge is due to the heat liberated by the following reaction:

$4PbO + 2S \rightleftarrows 3PbS + PbSO_4$

This action is proportional to the quantity present, so long as there is sufficient sulfur available to properly cure the rubber, and to convert the litharge to lead sulfide and sulfate. About 1 per cent sulfur is required for every 7 per cent of litharge. At the point where the rubber is fully cured the free sulfur drops, but is never completely absent. Large amounts of litharge serve to prevent "blooming"; i.e., the coming to the surface of colloidal free sulfur in the form of a gray scum.

Red lead is more active than litharge, but should never be used because of its oxidizing tendency. White lead, that is basic lead carbonate, is also an accelerator. Compared with litharge it has a much lower specific gravity and considerable toughening action. Sublimed white lead has the following average composition:

$PbSO_4$	78.5%
PbO	16.
ZnO	5.5

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It has only slight curing action, but is also a good toughener.

Zinc oxide: This has but little accelerating power. As a toughener it surpasses all of the lead fillers, and is only exceeded in this respect by lamp black. Because of its slight catalytic effect, considerable quantities can be used without retarding the cure.

Miscellaneous: Some oxides have a catalytic action under special circumstances. Thus, iron oxide (3 to 8 per cent) is quite useful in batches containing brown substitute.

Golden antimony sulfide also finds considerable use. It has but small catalytic value. Its action is due mainly to free sulfur, which the technical product always contains.

Manganese oxide, MnO, and cuprous oxide, Cu_2O, are both good accelerators, but because of their marked oxidizing tendencies they cannot be used. In fact, as a general rule copper and manganese, in any form, must be kept out of rubber if the product is to be anything but worthless.

Molybdenum sesqui-oxide over 10 per cent and alkali over 3 per cent are negative accelerators. The behavior of alkali is especially interesting, owing to the extensive use of alkali shoddies. Up to ½ per cent it acts as an accelerator. Beyond this it retards, and at 5 per cent it is almost impossible to effect a cure. Nickel oxide is a negative accelerator, and vulcanization can be entirely prevented by its use.

ORGANIC ACCELERATORS

The use of organic accelerators dates from the discovery of synthetic rubber. This product cannot be vulcanized without the addition of some of the organic catalysers. On the substitution of natural for synthetic rubber equally successful results were obtained.

The trouble with synthetic rubber, and for a time with the plantation variety, was excessive cleanliness. They secured the rubber hydrocarbon, but certain so-called impurities, which Mother Nature places in the rubber latex, were carefully excluded. Para rubber, by the Amazon method of coagulation, contains all the elements of the latex evenly distributed throughout the mass. For this very reason it is still true that no rubber is the equal of "Highlands Fine Para.

The catalysers present in rubber latex are thought to be related to the proteins, perhaps decomposition products. All organic accelerators are nitrogen bearing, and many have amino groups. The function of the nitrogen seems very important. So far there are only two generalizations possible:

1. According to Ditmar, all organic bases having dissociation constants greater than 10^{-6} act as accelerators, irrespective of constitution.

2. At present only nitrogen bearing compounds are known as accelerators, and it seems that this element must be a necessity.

From a mechanical standpoint a catalyzer is most conveniently mixed when it has the following properties:

It should be a solid, capable of being very finely pulverized.

It should have a high boiling point, so as not to be vaporized during vulcanization. Such behavior would cause a spongy appearance; that is, "blowing."

For convenience I will classify the most important organic accelerators under the following heads:

1. Carbon bisulfide addition products with
   - (a) Aniline
   - (b) Dimethyl aniline
   - (c) Tetrahydropyrrole
   - (d) Dimethylamine
2. Ammonium compounds
   - (a) Ammonium borate
   - (b) Aldehyde ammonia
   - (c) Quaternary ammonium bases
3. Amino compounds
   - (a) Para-phenylenediamine
   - (b) Tetramythylenediamine
   - (c) Sodium amide
   - (d) Naphthylene diamine
   - (e) BB Dimethyl Δ methyltrimethyleneimine
   - (f) Trimethyleneamine
   - (g) Benzylamine
4. Piperidine and derivatives
   - (a) Piperidine
   - (b) Methyl piperidine
5. Quinoline and derivatives
   - (a) Quinoline
   - (b) Quinoline sulfate
   - (c) Quinosol
   - (d) Sulfuroxyquinoline
6. Miscellaneous
   - (a) Anthraquinone
   - (b) Urea derivatives
   - (c) Formanilides

CARBON BISULFIDE ADDITION PRODUCTS

With Aniline: One of the oldest accelerators known in this country is diphenylthiourea, or thiocarbanilide,

$$\begin{matrix} & \diagup NH.C_6H_5 \\ C & = S \\ & \diagdown NH.C_6H_5 \end{matrix}$$

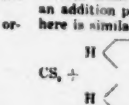
This substance may be prepared according to Gattermann as follows:

A mixture of 40 parts aniline, 50 parts carbon bisulfide, 50 parts of alcohol, and 10 parts of finely powdered potassium hydroxide are boiled gently on a water bath for three hours in a flask provided with a reflux condenser. Excess carbon bisulfide and alcohol are distilled off, and the residue treated with water. The crystals separating out are filtered off, washed first with water, then with dilute hydrochloric acid, and finally with water. To obtain the pure substance, recrystallization from alcohol is necessary. Large colorless tablets are obtained, which melt at 154 deg. C. A very satisfactory, and, in fact, a more desirable, product for use as an accelerator is secured by the substitution of sodium polysulfide Na_2S, for caustic potash in the above reaction. A high degree of purification is unnecessary. At some factories the aniline, carbon bisulfide, and sodium polysulfide are mixed in large kettles in the open air. After a short time the whole mass solidifies. This is broken up, vacuum dried, and finely ground. A fairly satisfactory product is thus secured. The reaction taking place in this preparation may be written as follows:

$$CS_2 + 2C_6H_5NH_2 = C \begin{matrix} \diagup NH.C_6H_5 \\ = S \\ \diagdown NH.C_6H_5 \end{matrix} + H_2S$$

This substance is a very efficient catalyser. It seems to do all of its work at the beginning of the reaction, so that it finds considerable use in quick curing stocks. One-half to 3 per cent is customary.

With Dimethyl Aniline: Carbon bisulfide also forms an addition product with this substance. The reaction here is similar to that of aniline.



With Tetrahydropyrrole: This substance $(CH_2)_4NH$ called by the German chemists "pyrrolidin," is secured

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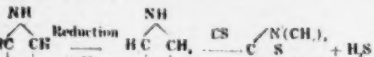
by the reduction of pyrrole, C_4H_5N, by means of zinc dust and hydrochloric acid. Pyrrole is closely related to the proteins, and its derivatives have been isolated from protein decomposition products. The reactions for the preparation of the addition product may be indicated as follows:



With Dimethylamine: As would be suspected, dimethyl amine, $(CH_3)_2NH$, gives an active addition product, whose constitution may be written: $C=S(N(CH_3)_2)_2$

AMMONIUM COMPOUNDS

Ammonium Borate: Dilmar (Gummi Zeitung, Jan., 1915) mentions the fact that ammonium borate has a noticeable effect on the cure. This is merely of scientific interest.

Aldehyde Ammonia: This is a very satisfactory catalyst. A mixture of 100 parts Para, 10 parts sulfur, and 1 part aldehyde ammonia may be cured in 30 minutes at 45 lb. steam pressure (140 deg. C.). For comparison, a batch of 90 parts Para, 9 of sulfur, and 1 of zinc requires 85 minutes at 140 deg. C.

Aldehyde ammonia, $CH_3CH(OH)NH_2$, is best prepared by passing dry ammonia gas into a solution of cold aldehyde, CH_3CHO, in ether. The reaction is as follows:

$$CH_3CHO + NH_3 = CH_3CH(OH)NH_2$$

It is readily soluble in water, sparingly so in alcohol, and almost insoluble in ether. It melts between 70 and 80 deg. C., and sublimes without decomposition at 100 deg. C.

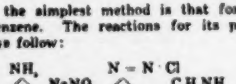
Quaternary Ammonium bases. These are mentioned in Bayer & Co.'s British patent 12,661 of May 22, 1914, along with aldehydic ammonia, para-phenylenediamine, sodium amide, benzylamine, and naphthylenediamine.

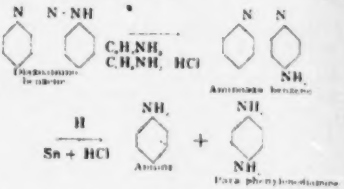
AMINO COMPOUNDS

Para-phenylenediamine: This accelerator gives good results with synthetic rubber. Bayer & Co. mention in their German patent 280,198, Jan. 1, 1914, that 100 parts isoprene rubber completely cures when mixed with 10 parts sulfur and 2 parts para-phenylenediamine and is heated in a press for 15 minutes at 45 lb. steam pressure.

Para-phenylenediamine, $C_6H_4(NH_2)_2$; is produced by reduction of para-nitrobenzene, para-nitraniline, or of aminoazobenzene with tin and hydrochloric acid. Other methods are: By the distillation of diamino benzoic acid. By the action of para-chloraniline on aqueous ammonia in the presence of copper salts.

Perhaps the simplest method is that for reducing aminoazobenzene. The reactions for its preparation from aniline follow:





This method is the most satisfactory, and relatively cheap. Gatterman may be followed for the preparation of aminoazobenzene. After reduction, distill off the aniline with steam. The product may be purified by fractional crystallization. Pure para-phenylenediamine melts at 140 deg. C., sublimes without decomposition at 267 deg. C., is very soluble in alcohol and ether, and moderately so in water. Manganese dioxide and sulfuric acid convert it to quinone, $C_6H_4O_2$. On passing hydrogen sulfide through a solution of the chloride, and then adding ferric chloride, thionine or Lauth's violet is produced. These tests will indicate the purity of the commercial article.

It should be mentioned that para-phenylenediamine, as likewise most organic accelerators, is very poisonous, and proper precautions should be taken in every case.

Tetramethylenediamine: This substance is mentioned in French patent 464,533 by Bayer & Co. It gives very good results when the desired time of cure is rather long.

Tetramethylenediamine, $NH_2(CH_2)_4NH_2$, called sometimes putrescine, is a natural product of protein decomposition, and is produced during the putrefaction of animal matter, such as flesh.

Dimthylene bromide, $Br.CH_2.CH_2.Br$, is converted by treatment with potassium cyanide to dimethylene cyanide, $NC.CH_2.CH_2.CN$. On reducing this substance with sodium and boiling alcohol or by electrolytic methods, tetramethylene diamine is secured.

$$NC.CH_2.CH_2.CN + 8H = NH_2(CH_2)_4NH_2$$

The crystals melt at 270 deg. C. and boil at 157 deg. C.

Miscellaneous Amines: Sodium amide, $NaNH_2$; naphthylenediamine, $C_{10}H_6(NH_2)_2$; trimethylene amine, $(CH_2)_3N$; benzyl amine, $C_6H_5.CH_2.NH_2$; 33 dimethyl 5 tr.methyleneimine; and nitrosodimethyl aninethylline are mentioned as having some accelerating power.

PIPERIDINE AND DERIVATIVES

The first patent granted for an organic accelerator was to Bayer & Co. (German patent 265,221, Nov. 16, 1912) for the use of piperidine. As above mentioned, it was intended to be used with synthetic rubber, but proved so successful that it was tried with the natural variety. A mixture of 100 parts Para, 10 parts of sulfur, ½ part piperidine, is perfectly cured on heating for 15 minutes at 53 lb. steam pressure. Without the accelerator over an hour is required. Piperidine is valuable for both hard and soft rubber articles.

Piperidine, $C_5H_{11}N$, belongs to the class of secondary amines. It is a liquid smelling like pepper and ammonia. It boils at 105.7 deg. C., and has a specific gravity of .881 at 0 deg. C. It is miscible with water in all

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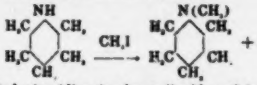
proportions. It is best prepared by reduction from pyridine, either by use of sodium in absolute alcohol or by electrolytic methods (E. Merck, English Pat. 21,471). The reaction is as given on the preceding page.

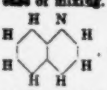
Methyl piperidine: This substance, $C_5H_{10}N(CH_3)$, is also active as a catalyser. It may be prepared by treating piperidine with methyliodide, when the amino hydrogen is replaced by the methyl group.



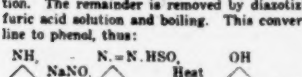
Methyl piperidine is also a liquid, and boils at 107 deg. C.

QUINOLINE AND DERIVATIVES

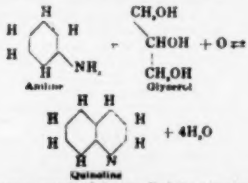
Quinoline and its derivatives are satisfactory accelerators. The amount used varies around 2 or 3 per cent. Perhaps its sulfate and quinosol find the greater application owing to ease of mixing.

Quinoline C_9H_7N,  , may be considered

as a combination of a benzene and pyridine ring. It is most satisfactorily prepared by Skraup's synthesis; to a mixture of 19 parts aniline, 12 parts nitrobenzene and 60 parts glycerol; 50 parts of concentrated sulfuric acid are added. Heat under a reflux condenser until reaction begins. Discontinue. When the energetic reaction is over, heat on the water bath for three hours. Cool, dilute with water, steam distill to remove any unchanged nitrobenzole. Make alkaline, steam distill off the liberated quinoline and any unchanged aniline. Considerable of the aniline can be removed by fractional distillation. The remainder is removed by diazotizing in sulfuric acid solution and boiling. This converts the aniline to phenol, thus:



Quinoline, being a tertiary amine, is not affected. On making alkaline phenol goes into solution, and quinoline is liberated. It can now be removed by steam distillation, after which it is fractionated in order to obtain the pure substance. The reaction for the production of quinoline is sometimes written as follows:



The oxygen required is supplied by nitrobenzole in a manner not quite clear.

Quinoline, sometimes written $C_9H_7\langle{CH:CH \atop N=CH}$ has a sp. gr. of 1.0947 at 20 deg. C. It boils at 240 deg. C., is soluble in alcohol and ether, but only sparingly so in water. It has a disagreeable, penetrating odor, a bitter, acrid taste, and on exposure to moist air is converted to the hydrate, $C_9H_7N + 1\frac{1}{2}H_2O$. The nomenclature of quinoline derivatives is indicated by the scheme

Quinoline sulfate: This is sometimes called quinoline sulfonic acid. For this purpose the 8-acid is most commonly used. It is secured on heating with concentrated sulfuric acid at 220 to 230 deg. C. for a short time. Perhaps the potassium salt of this acid would give better results.

Hydroxy quinoline: This quinoline derivative should be valuable as an accelerator. It may be prepared by the fusion of the 8-quinoline sulfonic acid with caustic potash. It forms prismatic needles melting at 76 deg. C., and boils at 266.6 deg. C. under 752 mm. pressure. It is sparingly soluble in cold water, readily so in alcohol, and volatile with steam. Aqueous solutions of its acid and alkali salts are yellow.

Quinosol: This is 8-hydroxy quinoline, 5-sulfonic acid, and is prepared by sulfonating 8-hydroxy quinoline with cool, fuming sulfuric acid. (Claus and Posset, J. pr. Chem. 1890, 2, 41, 33). Thorpe (Dict. App. Chem. vol IV, 471) prepares it by heating 8-hydroxy quinoline in alcoholic solution with potassium pyrosulfate, $K_2S_2O_7$. Quinosol forms small sulfur yellow needles, melting 175 to 177.50 deg. C. It is soluble in alcohol and in water.

Ditmar mentions oxyquiniline sulfide as a very satisfactory accelerator.

MISCELLANEOUS

Anthraquinone, 3 to 5 per cent is recommended for use in batches containing substitute.

Urea and such derivatives as guanidine are advised.

There are numerous patents covering the various anilides, such as formanilide, etc. Formanilide $C_6H_5.NH.CH:O$, is prepared from aniline and formic acid. On treatment with diphosphorpentasulfide, P_2S_5, thioformanilide is produced, $C_6H_5.NH.CH:S$.

Albumen: An interesting consideration is the patent of W. Esch (German patent 273,482, Nov. 22, 1912), which covers the direct addition of proteins to rubber. He first prepares a paste by mixing the protein, usually egg albumen, 15 parts, with 2 parts hydrated lime or magnesium hydroxide. This paste is mixed with the rubber, dried, sheeted, and smoked, to render the albumen insoluble. Low-grades are considerably improved.

CONCLUSION

To the casual reader this paper must appear rather rambling. I have only been able to touch the high spots in the subject of accelerators. In fact, only the high spots are known. As is customary with most great advances, the untrained investigator tries everything he can possibly think of. The theoretical man follows in his path, and adds his discoveries to the great mass of accumulated facts called "Science." The whole subject of rubber is one demanding scientific treatment. The velocity of the reaction between sulfur and rubber should be investigated more thoroughly and from the standpoint of the physical chemist. In fact, a consideration of this subject along the line of the phase rule would doubtless prove as valuable here as it did in the steel industry.

To the novice in this field patience is most necessary. No substance should be rejected until it has been tried under all possible conditions, and in all possible variations. In this, as in other lines of scientific research, the motto must always be, "Go as far as you can see, and then see how far you can go."

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of the high speed of passage of the reaction gases over the catalyst, a relatively small catalyst chamber will suffice for the oxidation of a comparatively large amount of ammonia per hour, and that secondly, since practically no power is required for the operation, the actual conversion costs, exclusive of that of the materials necessary, will be low. The power required for the production of one ton of nitric acid from ammonia should not exceed 0·015 kilowatt-year, exclusive of the cost of condensation and of concentration, a process which we are carrying out economically without the use of sulphuric acid.

Finally it may be of interest to compare, from a point of view of power, the relative efficiencies of the three most important methods for the fixation of atmospheric nitrogen, namely, the arc process, the cyanamide process, and the direct synthesis of ammonia from its elements.

In making such comparison it will be seen that in the arc process electrical energy alone is involved, while for the direct synthesis of ammonia a mixed requirement of coke (for hydrogen production, steam generation, etc.) and of power (for compression, etc.) is involved. Thus in order to obtain comparative figures it is necessary to translate the coke and other fuel required per ton of fixed nitrogen into units of power. The power equivalent of one ton of coke or coal is the number of units of electrical power which that ton of fuel would be capable of producing if it were utilised for that purpose under efficient conditions. This may be taken at 1500—1600 kilowatt-hours or 0·18 kilowatt-year.

By the arc process one kilowatt-year of power will produce about 600 kilos. of nitric acid or 130 kilos. of fixed nitrogen. For the production of one ton of fixed nitrogen (as cyanamide) by the carbide-cyanamide method, about two kilowatt-years of power plus 3—3½ tons of coal and other fuel are required, making a total power (converting coal into kilowatt-years as above) of 2·6 kilowatt-years per ton of fixed nitrogen. In other words one kilowatt-year by the cyanamide process will fix 380 kilos. of nitrogen as compared with 130 kilos. by the arc process.

Turning to the power required for the direct synthesis of ammonia, 6½—7 tons of fuel (coke and coal)* are required for the generation of the necessary hydrogen and for the production of all power required for the fixation of one ton of nitrogen as ammonia, including the separation of the nitrogen itself from the atmosphere. Converting fuel into power, as before, about 1·2 kilowatt-years are required for the fixation of one ton of nitrogen by direct synthesis of ammonia. Thus one kilowatt-year will fix about 830 kilos. of nitrogen, compared with 380 by the cyanamide method and 130 by the arc process. These figures mean that from the point of view of power and material the direct synthesis of ammonia is more than twice as efficient as the cyanamide process, and more than six times as efficient as the arc process.

These striking results are modified slightly by the difficulty in operating the direct synthesis and by the cost of labour, which is lighter than for cyanamide, together with the necessary dead charges, which are heavier. The direct synthesis of ammonia, however, accompanied where necessary by its subsequent oxidation to nitric acid, presents by far the most economical method of fixing nitrogen at present known, and if only by virtue of the urgent need of the land for cheap, abundant, and non-seaborne fertilisers, deserves every attention from a standpoint of national economy.

Discussion.

Mr. Morley remarked that many statements had appeared recently about the danger of explosion in connection with the Haber process, and he asked if it was possible to make a practical apparatus which would reduce this danger to a minimum. Whilst it was known that the process was practicable on a small scale, with retorts of a capacity of 300 or 400 c.c., he wished to know what was the largest size of retort which could be made commercially.

Mr. Mason asked whether, if it were possible to get cheap power, electrolytic hydrogen would be a possibility.

Mr. Webb asked whether Dr. Maxted adopted the ordinary system of absorption by means of the water towers, or whether an alkali separation or some other system was used.

Dr. Maxted, in reply, said the danger of an explosion as distinguished from a burst could be avoided. The Germans were making ammonia to the extent of a million tons a year by the process. With regard to electrolytic hydrogen, he pointed out that most gases which would generate power would generate hydrogen, and it would be more economical to use them in the latter way. His firm was not using the usual absorption method.

THE CHEMISTRY OF VULCANISATION.

BY D. F. TWISS, D.SC., F.I.C.

Introductory.

Although the hydrocarbon nature of rubber was realised before the discovery of the process of vulcanisation, analysis in approximate agreement with the empirical formula C_5H_8 having been made as early as 1822,[1] the careful examination of purified rubber, both from the point of view of composition and of chemical behaviour, was not taken in hand until years after vulcanisation had become an important technical process. Possibly to some extent because of this delay, but also very largely on account of the difficulties of accurate chemical investigation with a non-crystalline substance which is obtained chemically pure only with exceedingly great difficulty and is affected in a remarkable degree by mechanical treatment, there remain yet many points in connection with the rubber industry of which the scientific interpretations are contradictory, vague, or based on quite insufficient evidence. Nevertheless, more especially during the last ten years, extraordinary advances have been made in the chemistry of rubber.

As was first clearly demonstrated by Gladstone and Hibbert[2] the unsaturation of the caoutchouc molecule is such that two atoms of chlorine or bromine may be added for each C_5H_8 group present, any further introduction of halogen occurring only by displacement of hydrogen. More definite information as to the intra-molecular structure of rubber was supplied by the investigations of Harries. As a result of these and other researches the caoutchouc molecule is to-day regarded as composed of a succession of $-CH_2.C(CH_3):CH.CH_2-$ groups linked together into a ring of uncertain dimensions.[3] This constitution is in good accord with the possibility of the polymerisation[4] of isoprene, $CH_2:C(CH_3).CH:CH_2$, to caoutchouc, the movement of the double bond being commonly observed in a conjugated system of ethylenic linkings $-C:C.C:C-$ on the addition of a univalent atom or group at the first and fourth carbon atoms.[5]

As would be expected of an unsaturated hydrocarbon (C_5H_8)$_x$, containing an ethylenic linking in each C_5H_8 group, caoutchouc forms additive compounds with many of the reagents for olefinic substances, *e.g.*, with the halogens[7], the halogen hydracids[8], "nitrogen trioxide"[9], nitrogen dioxide[10], ozone[11], and chromyl chloride[12].

It is at first sight almost surprising that until recently so few of the reagents for olefinic compounds

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have been even tentatively suggested as agents for vulcanisation. The use of chlorine, bromine, iodine, and aqueous hypochlorous acid was suggested fairly early for this purpose[13], whilst in more recent years, benzoyl peroxide, which might be expected to react additively at a double bond as its parent compound hydrogen peroxide is known to do, and various aromatic nitro- and polynitro-compounds, which are known as a class to form additive compounds with olefinic substances[14], have been stated to convert rubber into a condition resembling vulcanised rubber[15]. The resemblance, however, is so remote that no serious hope can at present be entertained for a successful application of these substances to technical vulcanisation, although the result is certainly of interest, as showing that such reagents can produce a change in the physical characteristics of raw rubber.

The general chemical behaviour of caoutchouc would lead to the expectation that this substance would react fairly readily with sulphur chloride and also with sulphur, the former of which has for many years been known to yield additive compounds e.g., $(C_5H_8)_2S_2Cl_2$, with olefines[17]. As is well known, the technical vulcanisation of rubber is invariably effected by one or other of these substances. Additional ingredients may be and commonly are added to the rubber in order to ensure desired physical characteristics such as colour, definite specific gravity, coarseness, strength, or even (in the case of vulcanisation with sulphur) increased rate of vulcanisation, but the vulcanising effect itself is produced by sulphur or sulphur chloride. At a casual glance it is sometimes possible to overlook the presence of sulphur in some published rubber mixings on account of its introduction in "antimony sulphide" or "black hypo" containing a considerable proportion of free sulphur or as some proprietary "vulcanising compound" such as an intimate mixture of sulphur and wax.

Cold vulcanisation.

Vulcanisation by means of sulphur chloride is effected at or near the ordinary temperature and is restricted to thin rubber material. The material is dipped into a solution of sulphur chloride in some suitable inert solvent or is exposed to the vapour of such a solution. Parkes, who discovered the method in 1846, used a solution in carbon bisulphide.

Various investigators have submitted this process of "cold vulcanisation" or "cold cure" to scrutiny. An obvious difficulty in the way of accurate interpretation is the fact that cold vulcanising as technically practised is largely restricted to the surface layers and is not uniform in effect at various distances below the surface of the rubber. In consequence of this, the research methods employed have in some cases necessarily deviated somewhat from the technical conditions, the most definite results having been obtained from the action of excess of sulphur chloride on purified rubber in solution in benzene[18], when, whatever the excess of sulphur chloride applied, the product approximated to the composition $(C_{10}H_{16})_2S_2Cl_2$, which is analogous to that of the additive compound derived from sulphur chloride and the simple olefines, such as ethylene itself (see above). In view of the complications likely to arise from the presence of organic impurities natural to raw rubber and from the liability of sulphur chloride to vary in composition and to be affected by even slight traces of moisture which may cause the formation of insoluble sulphur (see later), the rather divergent results of earlier investigators[19] are not surprising. There can be no reasonable doubt that the action of sulphur chloride on rubber in cold vulcanisation is definitely chemical and that the final product is a compound of the composition just stated. As to what may happen to the general mass of rubber when in technical practice a piece of rubber almost is allowed to combine with a quantity of sulphur chloride quite insufficient to convert it wholly into the final additive product, is largely a matter of speculation which receives further mention below.

Heat vulcanisation.

The discovery of the great improvement in the mechanical properties of rubber induced by mixing with sulphur and submitting to a temperature between 135° and 140° C. (Goodyear, 1839) or by dipping the rubber articles into molten sulphur (Hancock, 1843) preceded Parkes' discovery of cold vulcanisation, but although the process of "heat vulcanisation" or "heat cure" is more general, its phenomena are even more complex and obscure.

That the chemical process in heat vulcanisation is purely additive was clearly demonstrated by Weber[20] who was also able to show that the limit of vulcanisation is reached when the proportions of rubber and combined sulphur approximate to the formula $C_{10}H_{16}S_2$, an observation which has received definite confirmation from the results of several other investigators[21]. Weber's views as to the formation of definite intermediate compounds, based on the assumptions that 2% forms a minimum proportion of sulphur for a satisfactorily vulcanised soft rubber and that certain discontinuities in his curve showing the percentage of combined sulphur plotted against the period of vulcanisation at constant temperature were of real significance, have, however, proved to be incorrect and due mainly to inaccuracies inherent to his experimental method. The course of the vulcanisation process under constant conditions is quite regular and smooth, the rate of combination of rubber and sulphur decreasing quite gradually as the amount of available free sulphur (and rubber) diminishes[22].

Although the process of heat vulcanisation presents a more complex problem than that of cold vulcanisation, it lends itself much better than the latter to scientific investigation on account of the possibility of so selecting the temperature that the reaction proceeds with conveniently measurable velocity. The velocity of combination of sulphur and rubber is increased by raising the temperature, the temperature coefficient[23] of approximately 2·7 for 10° falling within the usual limits of the value for a chemical reaction.

The phenomena during the heat treatment of a mixture containing rubber and sulphur will obviously include physical changes such as the melting of the sulphur and the dissolution of the molten sulphur in the rubber; by the latter the sulphur will become more uniformly diffused throughout the rubber, whereas previously it was localised in solid particles[24]. Indeed, in the Hancock process it is evident that the diffusion of the molten sulphur into the rubber must form an essential preliminary stage to vulcanisation beneath the surface. The melting and dissolving of the sulphur[25] have been followed under the microscope as also has the inverse crystallisation of the excessive dissolved sulphur[26], the latter, indeed, being well known in the so-called "blooming" or "sulphuring up" of heat vulcanised goods containing a considerable quantity of uncombined sulphur.

The adsorption theory.

With an additive chemical reaction between sulphur and a colloidal substance like rubber accompanied by a reversible solution process, the periodic recurrence of the suggestion that the vulcanisation process is not chemical but merely a physical adsorption phenomenon, is not surprising. In 1910, Wo. Ostwald[27] revived this theory with all the available favourable evidence, and his paper has caused the evidence to be sifted so thoroughly as entirely to dispose of the idea that vulcanisation can be a purely physical change. Ostwald's paper consisted of a review of the work of a few

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earlier investigators with an explanatory commentary biased in favour of the adsorption theory. Most of the arguments, however, suffer under close examination[39] and have received severe criticism, especially by Loewen[40]. Apart from accepting and applying to the purpose of his theory the peculiarities in Weber's experimental results which have since been proved to be due to mere inaccuracies and not to any corresponding abnormalities in the behaviour of the rubber-sulphur mixing[41] Ostwald's claim that vulcanisation is reversible,* based on the earlier statement of Höhn, is not in accord with the present impossibility of reproducing "raw rubber" by the "regeneration" or "reclaiming" of vulcanised rubber (see later), whilst his calculation that the results of Hinrichsen and Stern[42] and of Hübener[43] on the combination of rubber and sulphur are in agreement with the adsorption formula $\frac{x}{a} = kc^{\frac{1}{n}}$ where x represents the quantity of sulphur absorbed, c the original concentration of the sulphur, and a the quantity of the adsorbent, whilst k and n, are constants, is vitiated by the fact that he has misunderstood the figures quoted by Hübener from Hinrichsen and Stern and has used for the calculation figures corresponding in reality with an equation $\frac{x}{a^2} = kc^n$. The correct figures are no confirmatory of the view that the process is one of adsorption[39]. In like manner, the statement that in vulcanisation the sulphur never passes entirely from the free condition has been proved incorrect[44], whilst the remarkable alteration in physical properties observed in the formation of vulcanite and the fact that vulcanised rubber yields a bromo-derivative[45] and a nitrosite[46] containing combined sulphur, are great obstacles in the way of the acceptance of the purely physical conception of vulcanisation. Ostwald's sweeping assertions with respect to the nature of vulcanisation have caused the chemists to establish their faith on a firm experimental basis, and have thereby served to strengthen the position of the chemical theory.

Other theories.

Various modifications of the chemical theory of vulcanisation have been suggested. Erdmann proposed the explanation that sulphur acts on rubber in a triatomic condition, which he describes as thiozone by analogy with ozone; this theory[35], however, lacks experimental confirmation and, in the light of our knowledge of the allotropic forms of sulphur, is improbable.

Although the occurrence of chemical reaction between rubber and sulphur during vulcanisation cannot well be denied, this change may not be exclusively chemical in nature, and endeavours, with much in their favour, have been made to represent vulcanisation as a combination of a chemical change with an adsorption process. The suggestion that the free sulphur is adsorbed before vulcanisation[39], appears unnecessary and is less attractive and less probable than that the chemical product of vulcanisation is adsorbed into the remaining rubber after its formation. Examination of various technical soft products vulcanised by the heat process shows that the amount of sulphur in combination with the rubber is variable[27], but almost without exception falls somewhere between the limits of 2% and 7% calculated on the rubber present. Bearing in mind that the only definite chemical product of heat vulcanisation is of the composition $C_{10}H_{16}S_2$ (see above) containing approximately 47% of sulphur calculated on the rubber, it is obvious that technically vulcanised rubber represents no definite chemical compound but probably a solution or adsorption product of a more highly vulcanised product, possibly $C_{30}H_{48}S_6$, in an excess of very slightly vulcanised or sulphur-free rubber, the physical characteristics of the latter being modified by the presence of the admixed compounds[34]. Ostromisslenski[47], indeed, who regards his experimental results on the effect of aromatic nitro-compounds and of benzoyl peroxide as favouring such a view of vulcanisation, states that the vulcanisation of raw rubber can be effected by the addition of a small percentage of already formed caoutchouc hydrochloride or tetrabromide and subsequent heating, but his conception of a satisfactorily vulcanised rubber is rather wide. According to this view, vulcanisation in the sense of the acquisition of new physical properties by the general mass of the rubber, although not independent of the chemical combination of sulphur with part of the rubber, occurs subsequently to this combination and the small proportion of additive compound produced may be regarded as the direct vulcanising agent acting by "catalysis." The alteration in the main portion of the rubber, consequently, would be accompanied by no change in composition and must be ascribed to some alteration in the molecular condition which may be a polymerisation. Axelrod[39] had earlier propounded a somewhat similar theory involving the assumption that vulcanisation comprises two processes, one of which is the combination of sulphur and rubber. As is well known, heat tends to soften rubber whereas vulcanisation tends to produce the contrary effect. In Axelrod's explanation, the vulcanisation process depends on a primary softening, commonly described as "depolymerisation" or in a less committal manner as "de-aggregation"[48] of the rubber, followed by a "repolymerisation" under the influence of combination with sulphur[42]. Colour is given to this view by the fact that after the whole of the free sulphur has disappeared into chemical combination, further heating produces a weakening and softening effect; this indeed occurs to a greater or less extent in the "reclaiming" or "regeneration" of vulcanised rubber scrap by heating with acid or alkali, in which the material is again rendered sufficiently soft and tacky to be incorporated afresh as a diluent in rubber mixings[49]. Whether the so-called depolymerisation and repolymerisation as postulated in Axelrod's theory actually do occur alternately and repeatedly is not proven and it is possible that the two processes are independent and merely concurrent. The likelihood of modifications in the physical nature and molecular condition of rubber during vulcanisation is heightened by the results of Harries, who has shown not only that ordinary raw rubber behaves as if composed of three mutually interconvertible varieties[23], but also that in ordinary soft vulcanised rubber the major portion of the rubber is not in combination with sulphur although it possesses different physical and chemical characteristics from raw rubber[26]. The very considerable change which occurs when a newly vulcanised rubber is allowed to "mature" indicates that the alteration in mechanical characteristics induced by vulcanisation may continue for a short time after the chemical change is complete[44].

This hypothesis of physical change as induced by the chemical action occurring in vulcanisation has been extended to the process of cold vulcanisation[45] in which the quantity of combined sulphur chloride is likewise quite insufficient to convert the rubber entirely into the final additive compound.

It should, however, be clearly realised that these views in no wise support the adsorption theory of Ostwald, whose claim was that no chemical com-

* For a reply to the alternative argument that an adsorption process need not be reversible, as instanced by the case of methyl violet and charcoal, see Hinrichsen, Kolloid. Chem. Ind. Kraft, 1911, 6, 245.

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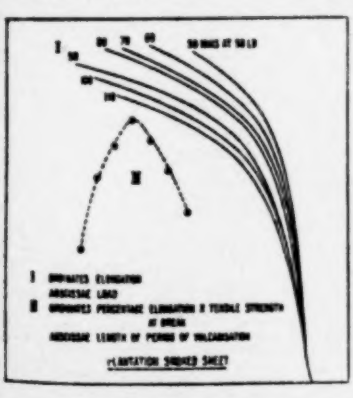
bination whatever occurred between the rubber and the sulphur, but that the latter was merely absorbed by a purely physical process.

Rate of vulcanisation.

The rate of vulcanisation of rubber is of importance for two distinct reasons. It is desirable in works practice that the period necessary for satisfactory vulcanisation should not be too prolonged, but on the other hand, it is very important that the behaviour of various consignments of rubber should be as uniform as possible so as to permit a standardisation of procedure without need for constant re-adjustment.

Examination of the rate of cure may be made from two points of view, viz., by measurement of the resulting physical effect[44] and by determination of the extent to which sulphur enters into combination when a mixing of standard composition is given a definite "cure." With a series of samples of rubber both methods as a general rule give results which fall into the same order, but the physical method possesses an advantage in simultaneously giving an indication of the inherent mechanical value of the rubber. Investigation from both points of view concurrently is certainly most satisfactory.

In the former method a standard mixing, frequently sulphur 10 : rubber 90, is adopted, and this is vulcanised for a series of gradually increasing periods at a constant temperature (*e.g.*, in steam under 50 lb. pressure), after which the mechanical properties of strength and stretch of the samples are measured, and the period of vulcanisation necessary to produce optimum mechanical properties decided from the results (see curves 1 and 2).



The coefficient of vulcanisation, *i.e.*,

$$\frac{\text{combined sulphur} \times 100}{\text{rubber}}$$

corresponding with the optimum period generally has a value of about 5, but it is improbable that such a coefficient would prove the most satisfactory for all purposes[45]. The results, however, are usually intended only for comparative purposes, and it is easy by their aid to detect a rubber of unusual quality either in mechanical strength or in rate of vulcanisation.

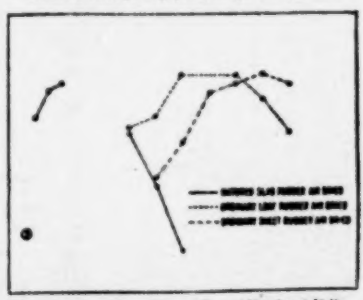
Natural accelerators.

Rubber is not a pure hydrocarbon substance, but is contaminated with natural resins[46] and protein substances[47], and it has been found that these foreign ingredients appreciably affect the rate of vulcanisation. If the resins[48] and more especially the protein matter[51] be removed from the rubber the rate of vulcanisation is decreased in a marked manner, whereas if rubber is enriched in natural proteins by dissolving away part of the rubber hydrocarbon with benzene, the rate of vulcanisation of the protein-enriched rubber is enhanced. Possibly as an outcome of this discovery, the addition of a mixture of lime and albumin[51] has been patented as a method for accelerating vulcanisation, but lime itself catalyses the vulcanisation process, and the increase in the rate of "cure" may not be due entirely to the albumin.

In the earlier days of the plantation rubber industry, considerable stress was laid on the variability in the rate of vulcanisation of "plantation Para" rubber as compared with the wild Para rubber. More recently, Eaton and Grantham, working in Malaya, have been able to discover the chief cause of this variability, and, indeed, to indicate the possibility of a step of great value in the production of raw rubber. In the ordinary plantation procedure, the rubber coagulum, obtained from the latex, is washed and crêped with the intention of removing the serum as completely as possible; if, however, the soft slabs of coagulum are allowed to "mature" for several days before the retained serum is expressed, it is found that the resulting rubber vulcanises with unusual rapidity, the effect attaining its limit after a period of roughly seven days before washing and crêping[52]. The rubber from such matured slabs when mixed with 10% of sulphur attains its optimum condition of vulcanisation in approximately one-third of the ordinary period.

Curves 3 and 4 show the behaviour of rubber prepared in this way as compared with the ordinary qualities of plantation rubber from the same estate; with the period of vulcanisation which gives the optimum results for the ordinary qualities, the special rubber is excessively over-vulcanised.

Tensile strength by percentage elongation.



The cause of this difference has been traced by Stevens[53], who has shown that during the maturing process, the protein matter of the retained serum undergoes decomposition with formation of organic bases which remain absorbed even after washing. Such bases are well known to possess considerable catalytic activity towards the heat vulcanisation of rubber (see later).

Although the difference in rate of vulcanisation as compared with rubber produced in the ordinary manner is less marked in technical mixings, the great advantage of a uniform supply of such rapidly vulcanising rubber for special purposes

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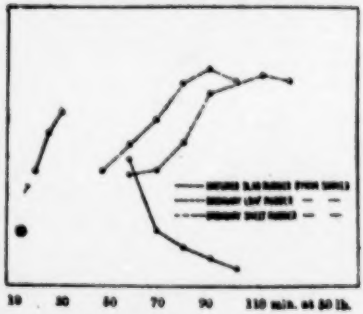
will readily be recognised, and experiments as to the possibility of producing large quantities of rubber with a uniform high rate of vulcanisation will prove of great interest.

Inorganic accelerators.

Goodyear himself realised that the process of vulcanisation could be hastened by the inclusion of calcined magnesia in the rubber-sulphur mixing, and the use of this substance, as also of litharge and calcium hydroxide (and, to a less extent, of magnesium carbonate), has for many years been a recognised device of the manufacturer to shorten the period necessary for the vulcanisation of his mixings. Various suggestions have been made to explain the effect of these substances, but few bear critical examination; thus conversion into sulphide followed by alternate formation and

Tensile strength by percentage at break.



decomposition of polysulphides, by which process the sulphide acts as a "sulphur carrier"[45], is improbable, because the corresponding sulphides are less efficient than the oxides or hydroxides, whilst it is also unlikely that magnesium oxide is largely converted into sulphide during vulcanisation; even the accelerating effect attributed to antimony sulphide[46] is largely due to misconception arising out of the effect of the free sulphur commonly present in this material.

Litharge has been a favourite subject for speculation. Its effect has been attributed, at different times, to its aiding the conduction of heat into the rubber mass[47], and to the heat evolved by its oxidising action on the rubber resins or on the hydrogen sulphide arising from the interaction of the resins and sulphur[47]. The rise of temperature due to such liberation of heat would cause a corresponding increase in the rate of reaction between sulphur and rubber, and it is probable that a thermal effect of this kind is produced by the direct or indirect action of the lead oxide on the sulphur[48]; the occurrence of a thermal effect in litharge mixings can indeed be detected by direct measurement of the temperature of the mass during vulcanisation.

A highly fanciful explanation of the effect of litharge and other oxide accelerators has been proposed lately[49]. The heating necessary for vulcanisation is assumed to cause the sulphur to attack the natural resinous matter and proteins and the litharge simultaneously, with formation of hydrogen sulphide and sulphur dioxide respectively. These two gases then react in the recognised manner, and the acceleration of the vulcanisation process is attributed to the exceptional activity of the amorphous sulphur thus produced. Apart from the improbability that two gaseous substances are formed in definite molecular proportions by independent chemical reactions as an essential part of the vulcanisation process, the facts that sulphurous acid and acid sulphites retard vulcanisation[50], and that colloidal sulphur does not give accelerated vulcanisation (see below) are diametrically opposed to this theory.

Apart from the above basic accelerators, the only inorganic accelerators which have been proposed are various metallic iodides, antimony iodide in particular[51]; in this case it is possible that the effect may have been due to the conjoint action of sulphur and iodine on the rubber; this method of acceleration appears never to have come into general practice.

Organic accelerators.

In recent years a notable advance in the technique of heat vulcanisation has been the introduction of organic bases as accelerators. The first published statement as to the use of an accelerator of this type appears to have been in the patent specification protecting the application of the strongly alkaline base piperidine, $C_5H_{11}N$ [52]; a claim by Spence to priority[53] in the use of this and other organic accelerators is still awaiting promised details. After piperidine, the use of many organic amines was patented[54], a final claim covering the application of all organic bases of dissociation constant exceeding 1×10^{-6}. It is inconvenient to apply some of these bases in the free condition on account of their volatility, which may cause loss by evaporation, or also may tend to produce porosity in the vulcanised rubber; this disadvantage may be obviated by previous conversion of the base into the corresponding carbamide[55], dithiocarbamate, carbamate, or carbonate derivative. Indeed, I have also found that the unstable base aminoguanidine forms an excellent accelerator when applied in the form of its more stable bicarbonate salt[56], while ammonium bicarbonate is also very effective.

One of the most powerful of these organic catalysts is aldehyde-ammonia, the effectiveness of which far outweighs what might be expected of its ammonia content, and must be regarded as a specific property of aldehyde-ammonia itself. Indeed, from the purely chemical point of view also, the behaviour of aldehyde-ammonia is somewhat abnormal, and although it must be regarded as a definite organic base its constitution is not settled beyond doubt[57].

It is a remarkable circumstance that almost the whole of the known effective* organic accelerators are basic, a rough proportionality apparently existing between their activity and their alkalinity, relatively feeble bases like aniline and methylaniline having little influence on the rate of vulcanisation. The mineral accelerators mentioned earlier are also alkaline or basic substances, and it appears highly probable that this is no mere coincidence but that the two classes of substances in common owe their influence in some way to their basic character. If this is really so, the alkali hydroxides should also be strong accelerators and experimental examination proves the correctness of this argument. For a long time it has been known that regenerated rubbers obtained by heating with alkali sometimes vulcanise with exceptional rapidity[58]; Martin[59] also has demonstrated that the introduction of a small percentage of powdered caustic potash into a mixture of rubber and sulphur causes a greatly increased rate of vulcanisation, whilst Eaton more recently has shown that a similar effect is produced with rubber which when freshly coagulated has been soaked in

* It is difficult to understand on what grounds certain substances have been described as accelerators; *e.g.*, see a list of accelerators by King, (Intelligence and Chemical Engineering, 1916, **18**, 231.

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caustic alkali solution. The latter investigation, however, has since withdrawn his recommendation of this process [70].

Several years ago, influenced by the fact that the inorganic and organic accelerators were all basic substances, I became of the opinion that both classes of substances exert their influence in a similar manner and that the relative advantage attaching to the use of organic bases depends chiefly, if not entirely, on the fact that these are soluble in rubber and therefore become more uniformly distributed and diffused, whereas the inorganic accelerators, being only sparingly soluble, remain for the most part localised in small solid particles, which, indeed, are frequently visible to the naked eye. For this reason I sought a suitable organic liquid which would dissolve in rubber and also would act as a solvent for an alkali hydroxide, because a solution of this kind would possess marked alkalinity and also would be capable of blending uniformly with rubber, thus reproducing the conditions which obtain when an organic accelerator is used, without any accompanying danger of porosity. The most suitable solvent discovered was glycerol which dissolves sodium hydroxide or potassium hydroxide, probably with formation of the corresponding glyceroxide [71]. The latter alkali is more easily soluble and a solution containing approximately 25% on the total weight is easily obtained. If 1–2% of such a solution (anhydrous) is introduced into a rubber-sulphur mixing, the vulcanisation process is greatly accelerated, the effect being comparable with that of the strongest organic accelerators, as is demonstrated by the figures below. It is also noteworthy that the actual quantity of alkali used approximates closely to the 0·5% recommended for the most effective organic accelerators and that with a rubber-sulphur mixing the resulting vulcanised rubber, in both cases, possesses the same clear, dark, almost semi-transparent appearance.

In earlier experiments, I had endeavoured to effect the uniform distribution of the alkali into the rubber-sulphur mixing by introducing it in the form of a finely-powdered mixture of the alkali with lime, but although the results were certainly gratifying, they were less consistent than those obtained with the glycerol solution.

The following figures give the residual uncombined sulphur after a mixing of 95 rubber : 5 sulphur with the addition of the stated accelerator was vulcanised for 90 minutes at 40 lb. steam pressure :—

Accelerator.	% of Accelerator.	Residual free sulphur %.
(1)	—	3·60
(2) Potassium hydroxide in glycerol	2 (of solution 1 : 4 approx.)	0·31
(3) Sodium hydroxide in glycerol	2 (of solution 1 : 8 approx.)	0·41
(4) Acetoguanidine	1	0·60
(5) Ammonium carbonate ..	1	1·39
(6) Aldehyde-ammonia	1	0·17
(7) p-Nitrosodimethylaniline	1	1·06

As will be observed from the above results, p-nitrosodimethylaniline [72] does not accelerate very strongly under the conditions chosen. This is due, at least in part, to the fact that the mixing selected contains a relatively low proportion of sulphur. The nitroso-compound is much more effective in mixings containing a high percentage of sulphur and it is probably because mixings containing litharge or antimony sulphide are usually intended to have a good colour and, therefore, in order to prevent excessive "blooming," are generally prepared with a low percentage of free sulphur, that these have been found to behave less satisfactorily with the nitroso-compound [73].

Mode of action of accelerators.

As the effect of accelerators in general is most distinct in mixings otherwise containing only rubber and sulphur, their action presumably must be by influence on one of the ingredients present, viz., (1) the natural protein and resinous matter, (2) the sulphur, or (3) the rubber hydrocarbon.

The first possibility is eliminated by the fact that the accelerators work equally well with rubber from which the protein matter has been removed, one of their first uses indeed being to render protein-free synthetic rubber capable of more rapid vulcanisation.

With respect to the possibility of acceleration as due to the influence of the catalyst on the sulphur, the suggestion has been made [74] that with organic, as with inorganic accelerators, polysulphides are first formed which then effect the vulcanisation of the rubber. As has been explained already, this theory is not altogether satisfactory for the effect of the basic oxides generally.

A possibility which appears to have been previously overlooked, but which at first appeals to the imagination, involves the two allotropic forms of liquid sulphur. Molten sulphur consists of a mixture of mobile yellow S_λ with viscous deep brown S_μ, the exceptional behaviour of molten sulphur with alteration of temperature being due to variation of the relative proportions of these constituents [75]. When molten sulphur is cooled, the S_λ variety gives rise to ordinary soluble crystalline sulphur, whilst S_μ produces insoluble amorphous sulphur. In molten sulphur an equilibrium is slowly attained between these two forms, but the existence of S_μ is favoured by the presence of acids, whilst alkalis such as ammonia or doubtless organic bases, facilitate the conversion of S_μ into S_λ.

The remarkable parallel between this effect of acids and bases on the $S_\lambda \rightleftarrows S_\mu$ equilibrium and that of acids and bases in respectively retarding and accelerating the vulcanisation process, naturally arouses a suspicion as to the existence of some connection between the two sets of phenomena. In order to test this possibility, insoluble amorphous sulphur corresponding with S_μ was separated from genuine flowers of sulphur by extraction of the soluble S_λ with carbon bisulphide. Comparative vulcanisation tests were then made with rubber-sulphur mixings employing this insoluble sulphur and ordinary totally soluble sulphur. Although my results actually indicated that S_μ combined with rubber rather more slowly that S_λ the difference was relatively slight and quite insufficient to account for the great effect of the organic basic accelerators.

Mixing.	Period of cure at 40 lb.	Residual free sulphur.
Rubber 100 : soluble sulphur 10	120 minutes	0·39
Rubber 100 : insoluble sulphur 10	120 "	0·61*

* This residual sulphur, after vulcanisation, is found to consist mainly of the more soluble modification.

Although this result disposes of the probability of any real connection underlying the parallel between the action of acids and alkalis in the $S_\lambda \rightleftarrows S_\mu$ equilibrium and in the process of vulcanisation, it is of additional interest as also disposing of Dubosc's suggestion that the action of inorganic catalysts in vulcanisation depends on the production of amorphous sulphur for which he postulates exceptionally great vulcanising activity [76].

The immediately preceding considerations to some extent narrow down the enquiry as to the mode of action of the basic accelerators. Either

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the sulphur is influenced in some other way than those mentioned, or the effect must be produced on the rubber itself. On account of the colloidal nature of rubber and its obscure "depolymerisation" and "polymerisation," the investigation of the latter alternative is more difficult. Nevertheless, the knowledge that alkalis increase the stability of the independent rubber globules[17] in ordinary rubber latex and the observation that even coagulated and worked rubber retains traces of a globuloid condition[27], might be regarded as suggestive of a possibility that alkalis are likely to affect the behaviour of finished raw rubber, *e.g.*, by influencing the inter-conversion of modifications in different states of molecular aggregation and of different reactivity. Such a possibility indeed, would be in accordance with C. O. Weber's observation[29] that when rubber is masticated with litharge only, in the absence of sulphur, the material undergoes a remarkable change in physical properties.

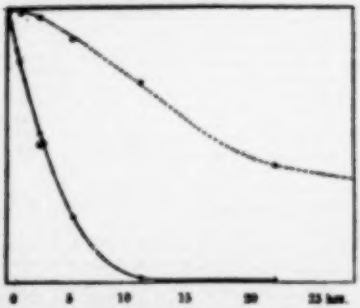
There is much more room for further investigation on the question of the chemical mechanism of the acceleration of vulcanisation.

Other considerations.

The existence of the above-mentioned soluble and insoluble modifications of sulphur is well worth bearing in mind in other directions. For instance, although it is generally accepted that the free sulphur in an ordinary rubber mixing can, for all practical purposes, be removed completely by continuous extraction for ten hours with acetone, the remaining sulphur being regarded as in combination with the rubber, the above unvulcanised mixing containing "insoluble" sulphur yielded only 27% of its sulphur in this period.

Comparative extractions were made with the two mixings containing respectively soluble and insoluble sulphur, by treating samples with acetone in a continuous extractor at the temperature of the boiling solvent; the rate of extraction is represented in the following curves.

Residual sulphur.



Any conclusions as to the reversibility of vulcanisation based on the possibility of removing sulphur from vulcanised rubber by prolonged extraction[30] even after as much as twenty hours' previous extraction, are, therefore, unjustified[31] unless definite proof is supplied as to the absence of "insoluble sulphur." It has also been stated by Bysow that in cold vulcanisation, sulphur and chlorine do not combine with the rubber in equivalent quantities[32], but traces of moisture in the rubber would cause the decomposition of part of the sulphur chloride with formation of some insoluble sulphur and would account for the apparently disproportionate quantity of "combined" sulphur.

The evidence for the supposed vulcanisation of a rubber-sulphur solution at the ordinary temperature by ultraviolet light[33] is also unconvincing. From the observation that a rubber-sulphur solution in benzene, when exposed in a thin film to ultraviolet radiation, becomes more viscous and that after evaporation of the solvent, part of the sulphur is not removed by an ordinary four-hour extraction with acetone, the conclusion has been drawn that the unextracted sulphur has combined with the rubber. However, ultraviolet light is already known to convert dissolved sulphur into insoluble sulphur[34] (or Rh into Rh) and although the Rh may not separate as visible particles it is quite likely to remain in ultra-microscopic colloidal suspension.* Ultraviolet light also, without the aid of sulphur can render rubber solution more viscous and improve the strength of thin rubber sheet[35].

The above alterations in the rubber-sulphur solution appear to be quite insufficient evidence of vulcanisation, and the observed changes, at least in part, may consist of independent physical changes in the rubber and sulphur respectively; indeed this possibility appears to receive some confirmation from Bernstein's doubts as to whether the sulphur in vulcanisation becomes chemically combined or merely physically adsorbed[36].

The preceding review of the chemistry of vulcanisation shows how great has been the activity in this direction, especially during recent years, but will also indicate how wide are the gaps of knowledge which at present are bridged over by mere theories and need to be filled up with a solid mass of experimental evidence.

Many of the results referred to in this paper as obtained by other investigators have been re-examined and confirmed.

For permission to publish the new results included, I am indebted to Dr. J. V. Worthington, Technical Superintendent and Director of the Dunlop Rubber Company, whilst for curves 1 to 4 and for many tests made in connection with points brought under consideration, I wish to express my indebtedness to Mr. A. W. T. Hyde, Head of the Physical Testing Laboratory of the same firm.

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DISCUSSION.

Dr. H. P. STEVENS said that he had carried out some experiments with benzoyl peroxide, but had obtained no results up to date which were really comparable with the results obtained with sulphur. On the other hand, he did not think his own research, at any rate, went sufficiently far to enable him to make the statement that benzoyl peroxide could not be used technically, and if Dr. Twiss had made experiments of his own, it would be interesting to hear what the results had been. A point often lost sight of was the effect of temperature on physical tests. In a paper read at the last rubber conference in London, an American investigator, Wormeley, had shown that variation of temperature produced a very large effect on the results of physical tests. He had found, for instance, that a difference in temperature of 20° F. a difference frequently met with in the test room between summer and winter—produced something like 10% difference in the tensile strength and elongation of the product. Up to now there appeared to be no appliance by which the temperature of the specimen during the test could be controlled. It was also important that previous to testing the specimen should be kept at a constant temperature. With regard to the rapidly vulcanising rubber produced by allowing the rubber to mature, he took it that such a rubber would be of greater value than the ordinary trade rubber as now supplied. During maturing oxidation took place, weakening the surface. It was interesting to hear of the author's experiments with the use of potash and soda. So far as he understood it, the results obtained with such an accelerator were in all respects comparable with those obtained with organic accelerators. There had been an idea that traces of alkali affected the stability, that was to say, the ageing qualities of rubber.

Dr. TWISS, in reply, said he had, as Dr. Stevens suggested, made experiments as to the possibility of vulcanising rubber with benzoyl peroxide and nitro compounds. The products did not compare in strength with technically vulcanised rubber. It seemed to him, however, that it was only a matter of time for substances to be found which would have an effect similar to that of sulphur chloride. As to the samples vulcanised in the presence of the alkali solution in glycerol, in the period that had elapsed since these mixings were vulcanised, now almost three years, a certain weakening was observed, but no greater than in similar mixings containing other accelerators used with considerable success by some manufacturers.

THE SCIENTIFIC NEEDS OF THE RUBBER INDUSTRY.

BY R. D. PORRITT, M.SC. (LOND.), F.I.C.

If statistics were available to show the numbers of men with scientific training absorbed annually by various British industries during the last twenty years, that of rubber certainly would be found to occupy a very humble position on the list, far below what might be expected in view of its commercial importance, and intricate character. Moreover, it would be apparent that until the last decade a chemist was practically unknown in the majority of factories engaged in this trade. Even at the present time a technical laboratory set aside solely for the purpose of research is a rarity, and the duties of the average rubber chemist still remain essentially what they

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REACTIONS OF ACCELERATORS DURING VULCANIZATION[1]

II—A THEORY OF ACCELERATORS BASED ON THE FORMATION OF POLYSULPHIDES DURING VULCANIZATION

By Winfield Scott and C. W. Bedford[2]

THE INVESTIGATION of organic accelerators, as shown by the literature of the past five or six years, appears to be confined largely to a search for new compounds, or a combination of compounds to catalyze the addition of sulphur to rubber. It has been shown that these accelerators are almost entirely organic nitrogen compounds, and as a result nearly all classes of nitrogen-containing substances have been tried. Furthermore, it has been shown that the nitrogen of such compounds is basic or becomes basic during vulcanization by the action of heat, sulphur, or hydrogen sulphide.

It has been previously proposed that a sulphur reaction of the accelerator is necessary, and certain reaction products in some way make sulphur available for vulcanization. In some cases a sulphur reaction is doubtless necessary to form the true accelerator, which is a polysulphide.

The latest theory for the action of accelerators during vulcanization is that of Kratz, Flower and Coolidge[3]. These writers attribute the accelerating action of amines, such as aniline, to the formation of an unstable addition product of aniline and sulphur, in which the sulphur is temporarily attached to the nitrogen, making it pentavalent.

The compound thus formed gives up its sulphur to the rubber and is then regenerated by a further reaction with sulphur.

The writer believes that the mechanism of the action of amines is represented differently from that given by the above investigators, and that hydrogen sulphide is one of the important factors in acceleration. It is believed that, in general, amines catalyze the addition of sulphur to rubber. As a specific example, dimethylamine, with hydrogen sulphide and sulphur, forms a derivative of ammonium polysulphide as follows:

$$(CH_3)_2NH + H_2S \longrightarrow (CH_3)_2NH_2SH$$

$$(CH_3)_2NH_2SH + xS \longrightarrow (CH_3)_2NH_2SH$$
$$\Big|\!\Big|$$
$$S_x$$

Polysulphide compounds similar to the above are considered to be the true accelerators that furnish the sulphur necessary for vulcanization. That this type of sulphur is available for vulcanization has been shown by Ignaz Block[4], who states that hydrogen polysulphides (H_2S_3 and H_2S_4) will cure rubber at ordinary temperatures. C. O. Weber[5] quotes Gerard and his work showing that alkali polysulphides in concentrated solution will also vulcanize rubber.

ORGANIC ACCELERATORS

All organic accelerators do not function in the same manner as the bases, and for this reason the writers choose to divide accelerators into two classes.

I. HYDROGEN SULPHIDE POLYSULPHIDE ACCELERATORS. In this class belong those bases which form polysulphides similar to yellow ammonium sulphide.

II. CARBO-SULPHYDRYL POLYSULPHIDE ACCELERATORS. This includes all accelerators that contain the grouping = C-SH, such as the thioureas, dithiocarbamates, thiurams, mercaptans or the disulphides which may be formed from them by oxidation or by reaction with sulphur.[6]

To the first class belong all basic organic accelerators or ... compounds as produce basic accelerators under curing conditions. Certain inorganic accelerators may also be included. These will be discussed later in the paper.

The second class includes certain of the Schiff bases[7] which form thiourea derivatives by a sulphur reaction during the cure. Further discussion of this class will be reserved for a later paper.

The phenylated guanidines belong to both classes, since at curing temperatures they easily react with hydrogen sulphide to form thioureas and free amines. Diphenylguanidine, for example, gives thiocarbanilide and ammonia.

The present paper deals with the first-mentioned class of accelerators, i. e., with those which, in the presence of hydrogen sulphide under curing conditions, form polysulphides analogous to those of sodium and ammonium.

The structural relationships of the polysulphides of the nitrogen bases and the more positive metals are not clearly understood at present, although it is known that some of the sulphur is held in a more or less loose form of chemical combination. This is evidenced by the precipitation of sulphur from concentrated solutions on dilution, and the generation of heat when soluble ... dissolves in sulphide or hydrosulphide solutions. It is certain that the sulphur of polysulphides is quite different from rhombic or α-sulphur, and that the aggregate S_8 is changed to the sulphur of polysulphides by the combined action of hydrogen sulphide and basic accelerators.

It is a well-known fact that sulphur will react with rubber resins and proteins at temperatures near 140 degrees with the formation of hydrogen sulphide. This hydrogen sulphide in the presence of basic accelerators forms hydrosulphides, which in turn take up sulphur to form polysulphides. These polysulphides pass on part of their sulphur to the rubber and constitute the true curing agents. Such a mechanism applies also to the cure by the action of alkali and alkaline-earth hydroxides. The fact that basic magnesium carbonate will react with hydrogen sulphide and sulphur in water suspension to form polysulphide solutions ... doubt accounts for its mild accelerating power. Lime and magnesia do not function well in deresinated rubbers where ... of the hydrogen sulphide producing materials have been removed. The sulphides and polysulphides of the alkali and alkaline-earth metals should function in deresinated or synthetic rubbers.

The relative accelerating power of the organic bases is dependent upon the facility with which they form polysulphides and the extent to which they are able to activate sulphur to make it available for the rubber. This will, in some measure be dependent upon the basicity. In a previous paper by the writers[8] it was stated that at least a part of the accelerating action of hexamethylene tetramine is due to the fact that during the cure there are produced, among other products, ammonia and carbon disulphide which, alone or with basic products present in the rubber, form dithiocarbamates. It may be added that "Ilex" also forms hydrogen sulphide by sulphur reaction, which with ammonia undoubtedly forms ammonium polysulphides. The accelerator may, therefore, be classed under both types since it both a hydrogen sulphide and a carbo-sulphydryl polysulphide accelerator.

Aldehyde ammonia, by the action of heat alone, forms ammonia while with sulphur it also gives hydrogen sulphide. Heat produces other bases such as the alkyl pyridines or collidine. This material appears to be solely a hydrogen sulphide poly...

[1]Presented before the Rubber Division of the meeting of the American Chemical Society, Chicago, Illinois, September 9-10, 1929. Part I, The India Rubber World, January 1, 1930, pages 294-297.

[2]The Goodyear Tire & Rubber Co., Akron, Ohio, and Quaker City Rubber Co., Philadelphia, Pennsylvania.

[3]Journal of Industrial and Engineering Chemistry, 12, 1928, 21.

[4]German patent No. 219 925.

[5]"Chemistry of India Rubber," page 47.

[6]Although the term polysulphide is applied to each class of accelerators, it should be noted that they are distinct types. In Class I, the polysulphide sulphur is related to a sulphydryl group attached to nitrogen, while in Class II the polysulphide sulphur is held by a sulphydryl group attached to carbon. In the so-called disulphides and their higher sulphides, the hydrogen of the sulphydryl group is considered as having been eliminated in hydrogen sulphide.

[7]Bedford and Scott, Journal of Industrial and Engineering Chemistry, 1929, 21.

[8]The reaction of carbon disulphide on amines to form thioureas or hydrogen sulphide is reversible, and it is entirely possible that by the action of hydrogen sulphide during vulcanization the thioureas are changed to more powerful dithiocarbamates which are intermediate to the cure by transformation to amine and carbon disulphide. It is also possible that thioureas may form polythio compounds direct, through the carbo-sulphydryl group.

[9]Journal of Industrial and Engineering Chemistry, 12, 1920, 21.

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ide accelerator. The ammonia condensation products of other ...dic aldehydes behave in a similar manner.

...-Phenylenediamine is an accelerator that is much more active ... would be assumed from its basicity. At curing tempera..., this accelerator reacts with sulphur to form large amounts ... ammonia and hydrogen sulphide together with certain weaker ...s. If the reaction be carried out under a cold reflux, the ...denser will frequently become clogged with the white solid ...pounds of ammonia and hydrogen sulphide which are described ... Rossze and Schorlemmer. The action of *p*-phenylenediamine ...de cure is entirely that of a hydrogen sulphide polysulphide ...elerator.

The three above-mentioned accelerators are not dependent on ... rubber resins or proteins for their supply of hydrogen sulphide, ...e this is one of their sulphur reaction products. It is to be ...ected that these accelerators will function in a deresinated or ...ynthetic rubber, and the Bayer patents state that this is true. ... also known that piperidine will cure in a nitrogen-free rubber. ...re we have a strong base acting apparently without the aid of ...drogen sulphide. Piperidine, however, reacts with sulphur at ...peratures lower than those used in vulcanization, with the ...mation of hydrogen sulphide. Both the sulphur reaction ...duct and the unchanged piperdine may then use this hydrogen ...phide to form polysulphides with sulphur.

INORGANIC ACCELERATORS

Inorganic accelerators that function in the cure by the removal ... hydrogen sulphide the writers choose to term "secondary accel...ors," while those that function in the same manner as the ...anic polysulphide accelerators may be classed with them as ...imary accelerators." A third class consists of those com...nds that are both primary and secondary accelerators.

I. Secondary Accelerators. Litharge, zinc, oxide, etc., seem ... act no further than to form the corresponding sulphides, in ...nction with hydrogen sulphide polysulphides.

II. Primary Accelerator. To this class belong the ...phides and hydrosulphides of the alkali and alkaline-earth ...tals.

III. Accelerators That Are Both Primary and Secondary. ...rganic oxides and hydroxides function first as secondary ac...erators forming sulphides or hydrosulphides which then take up ...phur and act as primary accelerators. Such accelerators are ...dium and calcium hydroxides, magnesium oxide and basic car...nate, etc.

Secondary accelerators are believed to function as aids to ...anic polysulphides by breaking them up into colloidal sulphur ... the original nitrogen base. This may be illustrated by the ...eterioration of polysulphide solutions by litharge or zinc oxide. ...nc oxide does not act as a secondary accelerator, and neither ...es it readily decompose the polysulphide solutions. The solu...ity of organic accelerators in sulphur and rubber gives them ...ch more intimate contact with hydrogen sulphide at the time ... its formation than is the case with the comparatively large ...rticles of litharge or zinc oxide. Hydrogen sulphide is there...re available for the formation of organic polysulphides before ...ng taken up by the secondary accelerators. The decomposition ... a polysulphide by a secondary accelerator regenerates the free ...e, which with more hydrogen sulphide and sulphur re-forms ... polysulphide. Secondary accelerators do not act as true ...lphurs; once formed into sulphides they do not react again with ...drogen sulphide.

SUMMARY

1. All organic accelerators are believed to function through ... formation of some type of polysulphide.

2. Organic bases and compounds that form bases during vul...nization are believed to form polysulphides through the aid of ...drogen sulphide. These are termed "hydrogen sulphide poly...phide accelerators."

3. Thiourea, dithiocarbamates, thiurams, and mercaptan com...nds are believed to form polysulphides directly, or by first forming disulphides, and are termed "carbo-sulphydryl polysulphide accelerators."

4. It is proposed that the function of such compounds as litharge and zinc oxide may lie in the decomposition of polysulphides into colloidal sulphur and amines.

5. Such inorganic compounds as sodium hydroxide, calcium hydroxide and magnesium oxide are believed to function as "primary accelerators" through the formation of inorganic polysulphides.

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DEFENDANT'S EXHIBIT S

Caoutchouc et Gutta-percha 1919, July 15, p. 9861/9864

Investigation of Vitalyzer - Accelerators

From our earlier investigations it follows that nitrogen-containing organic substances, e.g. amines or imines, capable of giving rise, in the presence of sulfur and carbon disulfide, to sulfocyanic acid and hydrogen sulfide, are apt to act as vitalyzer-accelerators in the vulcanization of rubber.

The representative type of these vitalyzer-accelerators is hexamethylenetetramine.

Other compounds are capable of acting in the same manner; those which we have investigated, such as guanidine, tetraminocarbenzylidineaniline, hydrobenzamide, naphthylenediamine, paranitrosodiphenylamine, the various nitrogen compounds, and particularly, cobaltamines, which are capable of holding as much as 10 to 12 molecules of NH_3, decompose at low temperature and are therefore capable of yielding absolutely new powerful vitalyzer-accelerators.

These compounds will be examined now in succession:

Guanidine: This compound belongs to the urea group and its formula is $\begin{matrix} NH_2 \\ NH_2 \end{matrix} \rangle C = NH$

containing three nitrogenous radicles for one carbonation.

In order to provoke its action in the vulcanization process it is necessary in view of its low carbon content to use it in conjunction with carbon bisulfide.

A reaction sets in accordance with the following equation:

$$(NH_2)_2\ C(NH) + 2(CS_2) = 3(SCNH) + H_2S$$

Guanidine — carbon bisulfide — sulfocyanic acid — hydrogen sulfide

The preparation of guanidine is readily effected.

It is obtained by the action of ammonium chloride NH_4Cl on calcium cyanamide.

The reaction is carried out in an alcoholic menstruum at 100°C. when there is formation of calcium chloride, ammonia, and

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guanidine, according to the equation:

$$CN_2Ca + 2(NH_4Cl) = (NH_2)_2C = NH + CaCl_2 + NH_3$$

Calcium cyanamide is a low-priced product which is derived from calcium carbide and used as fertilizer. It is manufactured on a large scale at Niagra Falls and in the Savoie.

By refrigeration guanidine is readily induced to crystallize from the alcoholic mother-liquor.

It forms hygroscopic white crystals.

It may also be prepared by heating at 180° C. ammonium sulfocyanide in an autoclave. Thiourea is formed simultaneously which is split into hydrogen sulfide and sulfocyanic acids.

The reaction takes place according to the following reaction:

$$2(CNSNH_4) = (H_2N)_2C = NH + CNSH + H_2S$$

Guanidine readily absorbs carbon dioxide from the air with formation of a carbonate which decomposes at 110° C. It is advisable therefore to keep it in sealed receptacles.

Instead of preparing the guanidine separately it is possible to mix its constitutive elements with rubber, e.g. either calcium cyanamide and ammonium chloride, or ammonium sulfocyanide, whereupon, after an intimate mixture has been obtained, carbon disulfide is added in the kneading mill. The resulting mixture is then vulcanized under the same conditions as with hexamethylenetetramine.

In this case better results are obtained with ammonium sulfocyanide than with calcium cyanamide and ammonium chloride, as in the ensuing reaction which then takes soluble place in two phases, all the products act as accelerating vitalyzers, whereas in the other case an inert substance, viz. calcium chloride is obtained as by-product.

The reaction is as follows:

$$2(CNSNH_4) + 2CS_2 = 4(CNSH) + H_2S$$

The results are in the main the same as those obtained from hexamethylenetetramine.

Ammonium sulfocyanide is readily obtained either by the Gelis or by the Norton method by causing carbon bisulfide to act in auto-

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clave on carbamide or, better still, on ammonium carbonate.

Ammonium sulfocyanide may also be readily recovered from the ammoniacal liquor of coke-over plants or gas-works. It is separated from the other ammonia compounds by treating it with copper s which precipitates copper sulfocyanide which is separated by filt

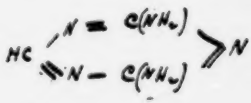
This copper salt is converted into the soluble barium sa barium hydroxide. The barium sulfocyanide is converted into ammo sulfocyanide by double decomposition with ammonium sulfate.

The resulting solution is then concentrated until crystal zation sets in.

Ammonium sulfocyanide, being very hygroscopic, should be in closed vessels.

Formoguanamine - Using guanidine as a starting material, series of compounds richer in nitrogen may be obtained to which th generic name "guanamines" is given.

One of the most readily obtained is formoguanamine which corresponds to the formula

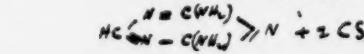


and contains 5 nitrogen atoms.

From the structural point of view this compound resembl hexamethylenetetramine, but is a pentamine.

Since it contains only three carbon atoms it is necessary to act upon it with carbon sulfide in the vulcanization process. I acts exclusively as a vitalyzer as it gives rise only to sulfocyan acid.

The reaction takes place according to the equation:



The preparation of formoguanamine is a very simple oper as the product is derived from the combination of guanidine with f acid.

Guanidine which has been studied above and is readily de from calcium cyanamide and ammonium chloride, is a very powerful b

COPY BOUND CL

ld readily combines with mineral and organic acids, yielding
only the corresponding salts.

Guanidine when treated with formic acid gives guanidine
ate $CH_5N_3.COOH$ which, on being heated, loses H_2O, CO_2 and NH_3,
gives rise by condensation of two molecules of guanidine formate,
form a guanamine $C_3H_5N_5$.

An entire series of homologous guanamines may be ob-
ed by substituting for the hydrogen of the CH group an alcoholic
ile such as, for instance, acetoguanamine

$$CH_3C\begin{matrix}/N=C(NH_2)\\ \backslash N-C(NH_2)\end{matrix}\gg N$$

ioguanamine

$$CH_3-CH_2-C\begin{matrix}/N=C(NH_2)\\ \backslash N-C(NH_2)\end{matrix}\gg N$$

Propioguanamine acts as vitalyzer-accelerator without
assistance of carbon disulfide giving rise to sulfocyanic acid and
gen sulfide according to the equation:

$$H_3-C\begin{matrix}/N=C(NH_2)\\ \backslash N-C(NH_2)\end{matrix}\gg N+7S=5(CNSH)+2H_2S$$

This product is therefore more practical than formo-
amine.

It may be prepared by causing propionic acid to act upon
dine; the resulting propionate crystallizes readily by sufficient
igeration.

The propionate, on being heated to 180-200° C gives water,
n dioxide and ammonia, and by condensation of two of its molecules,
ioguanamine.

Biguanide or guanylguanidine - This compound corresponds
e formula

$$HN=C\begin{matrix}/NH_2\\ \backslash NHC(NH)NH_2\end{matrix}$$

It contains 5 atoms of nitrogen for two of carbon, hence
t in the process of vulcanization only in the presence of CS_2.
action takes place according to the equation:

$$HN=C\begin{matrix}/NH_2\\ \backslash NHC(NH).NH_2\end{matrix}+3CS_2=5(CNSH)+H_2S$$

biguanide — carbon disulfide

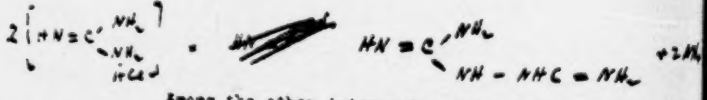
OSE IN CENTER

This is a vitalyzer-accelerator.

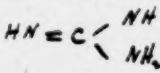
Biguanide is obtained by starting from guanidine hydrochloride. This salt is obtained by neutralizing guanidine with hydrochloric acid and concentrating the reaction product until crystallization sets in.

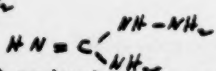
Guanidine hydrochloride crystallizes in stout white lamellae.

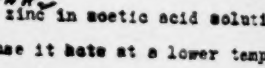
Guanidine hydrochloride, on being heated to 160-163°C., condenses two of its molecules into biguanide, by losing a molecule of ammonium chloride, according to the equation:



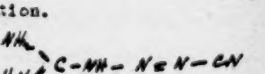
Among the other interesting guanidine derivatives which are capable of acting as vitalyzers, but are more difficult to prepare, mention should be made of nitrosoguanidine,



and of aminoguanidine  obtained by reducing nitrosoguanidine with powdered zinc in acetic acid solution, and forms an excellent vitalyzer because it acts at a lower temperature than the other guanidine derivatives.

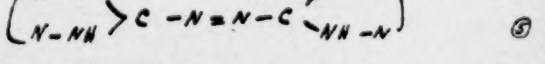
Azodicarbodiamidine: 

This compound which contains 6 nitrogen atoms results from the condensation of two guanidine molecules: it is of particular interest as a vitalyzer and acts in the presence of carbon bisulfide yielding 6 molecules of sulfocyanic acid. Unfortunately it is exceedingly difficult to prepare since one has to start from guanidine azonitrate which is a dangerous explosive.

Hydrazodicarbodiamidine 

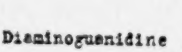
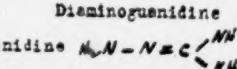
exhibits the same difficulties of preparation.

Diazoguanidine cyanide

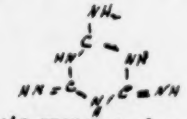
Azotetrazol 

COPY BOUND CLO

This compound contains 10 nitrogen atoms, and in the presence of formaldehyde or trioxymethylene and carbon bisulfide, might become an excellent vitalyzer: unfortunately its preparation is exceedingly delicate, and is not likely ever to be carried out on an industrial scale.

Diaminoguanidine  and triaminoguanidine  The latter substance is interesting as it contains 6 nitrogen atoms, but its preparation from ammonia, hydrogen and carbon tetrachloride is a very delicate operation.

Melamine- Melamine is a triamide derived from cyanuric acid and corresponds to the formula $C_3H_6N_6$.



It contains 6 nitrogen atoms; in presence of carbon disulfide it constitutes a vitalyzer which reacts according to the equation

$$C_3N_6H_6 + 3CS_2 = 6(CNSH)$$

Melamine + carbon bisulfide = sulfocyanic acid.

Melamine is readily prepared by polymerization of cyanamide, by heating it in an autoclave to 150° C. or else by rapidly heating ammonium sulfocyanide; it crystallises in prisms from its aqueous solutions whence alcohol or ether precipitate it as a fine powder.

Along with it three other compounds, likewise of interest as possible vitalyzers, always are formed. These are: melam $C_6H_6N_{10}$ which contains 10 nitrogen atoms $C_6H_6N_{10}$ which contains 11 nitrogen atoms; and melon $C_6H_3N_9$.

These compounds are formed when ammonium sulfocyanide is heated between 150 and 250°C.

As results from the above account the series of amino compounds derived from urea and cyanamide is capable of yielding vitalyzers which are rich in nitrogen and, consequently, exceedingly powerful.

A. DuBosc.

OSE IN CENTER

Sept. 16, 13.

Prepn of Diphenyl naphthyl guanidine. Ex P

Ex

Object - Howes thought that the above compd. sub
might result from the boiling of the AN mixture, th
as the activity of the boiled mixture was found to be
greater than that of the mix. mixed heated
was desired to prepare the above substance in the p
state and try it against AN mixture

Process - The following method as given

COPY BOUND CL

Beilstein II, 604, was used. (2)

14.3 g of α-naphthalamine and 22.8 g of β-carbamilide were dissolved in 500 cc. alcohol, and 30 g. PbO. added. The mixture was boiled in a ~~Erlenmeyer~~ for 3 hrs. No NH3 was given off. At the end of this time the major portion of the alcohol was distilled off and the substance allowed to crystallize out. The reaction was by no means quant. as only 6.0 gm of substance (m.p. 168°C) was obtained. It was a pure white, extremely light powder. The

SE IN CENTER

Purpn. of Diphenylnaphthylguanidine.

m. p. as given in Beilstein was 153°C. The remainder remained behind as a thick pink syrup.

Purpn. of Isomyde.- The white powder was made up into a compd. running ordinary V mixture as a control

	LN VII	PN. 6 VII	(94
White baryta	200	200	
Zinc oxide	200	200	
Sulphur	10	10	
Substance	6	6	

60 X 40 and 90 X 40 cures were made. Thumb tests did not show much difference between the activity of the two substances but if any was present the LN was the more active

Ex 6

(5)

Preparation of Diphenyl methylguanidine.

Testing of Slabs of Slabs were tested in Schoppen with following results.

	mm	Size of test plate	Kg	Elong.	
L N III	20×40	3.75×35	67.6	469	670
P.N.G. VII.	20×40	3.75×35	31.0	460	657

77) By heating monograph-this urea with P10 in absolute ammonia until P10 was no longer blackened. M.P. of product = 173°C.

H Cords

Def's Ex. No. D
U. S. Dist. Court,
S. D. of N. Y.
JA 2

Left Exhibit D
Oct. 1925
Mlo.

Def't 23

Relative Catalytic effect of Complexes. Related to S-Carbamide.
Preparation of the different Complexes.

Complexes were prepared by the following methods -
1.) - Technically pure.
2.) - From aniline Thiol
3.) - Mono phenyl thio urea from ph-mustard oil & ammonia
4.) - Heating NH_4CNS to 130° & cooling. fractionally.
5.) - By Condensation of ph-mustard oil prepd.
6.) - By heating S-carb. in alcoholic media. soln.
with PbO until latter was no longer blackened.

(35

Relative catalytic effect of benzyls. Related to S-test.

Other effects

Phenyl mustard oil found to be inactive.

A mixt. of equal mols. of aniline & the mustard oil, equal to 3% of the rubber, was active only to the extent of the aniline present.

A mixt. of equal mols. of aniline & S-carb equal to ($1\frac{3}{4}$ % TE) $3\frac{1}{2}$ % of the rubber was active only as to its constituents and not as to the phenyl guanidine

Ex 40

Relative bactericidal Effect of Compds. Related to 5 - Carbamidophthalic.
XI/1916.

The following formula was used to try out the activity of various substances more or less closely related to 5-carbamidophthalic —

White Cross 100
Zinc Oxide 100
Sulphur 5

The following effects were recorded and, in cases where an acidification was produced, the amt. required to give a cure in one hour equal to the cure produced by 3% 5-carbamidophthalic were as follows —

1) Aniline 3.5% 3) None through this area 1.5% (151 7-9)
2) 5-Carbamidophthalic 3.0% 4) This area 1.0 % (+) (area

5) Tri phenyl guanidine (SO) = 1.75%
6) Di " " = 0.25% - (146 6)
7) mono " " = 0.25% - (191-194)

Other Effects -

Phenyl mustard oil = inactive.

A mixture of equal mols. of aniline & phenyl mustard oil, equal to 3% on rubber, was active only to extent of aniline present.

A mixture of equal mols of aniline & S-carb equal to 3½% on rubber was active only to the extent of the S carb present.

Ex. 10.

Relative Catalytic Effect of Compds. more or less Closely Related to (3- Chloranil.

~~Cl₂DK~~. — M. T. TR. Leo. XI 1/11.

The following formulae was used to try out the activity of various substances more or less closely related to 3 Chlor

White Para 100
Zinc Oxide 100
Sulphur 5

The following effects were ~~observed~~ recorded and, in cases where an acceleration was produced, the amts. req'd to give a cure in one hr. equal to the cure produced

by 3% of S-Cerv., were as follows —

Urine	
24 hours Thio urea	= 3.5%
urine " "	= 5.0
Thio urea	= 1.5
24 hours guanidine (α)	= 1.0 (+)
" " (urea)	= 1.75
urine "	= 0.25
urea	= 0.25
	= 0 33

Ex 10

952

Oct. 31, 46.

Not.

Relative Catalytic Effect of Various Sulphur Compounds.

As S-carbamide gave a cure on the following compd. in 60×5·0 idea was to determine the amounts of the other substances necessary to be used in order to give same cure in same time.

	S.C.	P.S.C.	T.P.G.	A.	A+P.M.O.	A+S.C.	
White Para	200	200	200	200	200	200	200
Zinc Oxide	200	200	200	200	200	200	200
Sulphur	10	10	10	10	10	10	10
Substance	6	3	3·5	—	—	—	—
A.	—	—	—	7	2·5	2·2	1·1
P.M.O.	—	—	—	—	3·5	—	—
S.C.	—	—	—	—	—	5·8	2·9

	T.U. (M.P. 168°C)	D.P.G.	D.P.G. I.	D.P.G. II.	D.P.G. III.
White Para	200	200	200	200	200
Zinc Oxide	200	200	200	200	—
Sulphur	10	10	10	10	10
Substance	2	3	1	0·7	0·7

D.P.G. I. = M.P. of 147°C.
D.P.G. II. = M.P. of 149°C.
" III. = " " - .
" IV. = " " - .
M.P.G. V. = " " 173°C.
D.P.G4 = " " 157°C

D.P.G. V.	M.P.G.	D.P.G4
200	200	200
200	200	200
10	10	10
0·5	0·4	3

Of the White polymer products.

DF 1/12.

Exh.

Relative Catalytic Effect of Compounds Related to Sulpho Carbamide.

The following formula was used to try out the activity of various substances more or less closely related to sulpho-carbamide.

White Para	100
Zinc oxide	100
Sulphur	5

The following effect was recorded and, in cases where all accelerator was produced, the amounts used to give a cure in one hour equal to that produced by 3% of S-Carb., were as follows—

Aniline	=	3.5%
Di phenyl thio urea	=	3.0%
Mono- " "	=	1.5%
Thio urea	=	1.0% (+)
Tri phenyl guanidine (DC)	=	1.75%
Di phenyl guanidine (Lyon.)	=	0.25%
Mono-phe- guanidine urea	=	0.25%
	=	0.33%

Other agents —

Phenolised mustard oil = Inactive.

A mixture of equal mols. of aniline & phenolised oil, equal to 3% of the rubber, was active only to the extent of the aniline present.

A mixture of equal mols. of aniline & S- was equal to 3½% of the rubber was active only to the extent of the S-Carb. present

Nov. 3, 1916.

WAK.

Preparation of Di Phenyl Guanidine.

Prepn. carried on on the basis of the following reaction—

$$\begin{matrix} C_6H_5NH \\ C_6H_5NH \end{matrix}\!\!>C\!\!< + PbO + NH_3 \rightarrow PbS + H_2O + \begin{matrix} C_6H_5NH \\ C_6H_5NH \end{matrix}\!\!>C\!\!<NH.$$

228 (30) 223 211 (27.77)

30 g. of S-carbanilide was dissolved in 225 cc. strong alcoholic ammonia and 175 cc. of 95% alcohol and 30 g. of PbO was added to the S-carbanilide soln. and the mixture heated to gentle boiling for several hours.

At the end of this time the blackened PbO (PbS) was filtered off and a fresh 30 g. portion of PbO added. Boiling continued and allowed PbO stand over night; PbS filtered off. Fresh PbO added (20 g.) and boiling recontinued. The third portion of PbO did not blacken. soln. filtered free from PbS & PbO and concentrated. Taken down to a 200 cc. & no crystals yet in soln.

Di-ph-guanidine is supposed to be sol in alcohol 1:10

Recrystd. several times from alcohol; came out in beautiful large flat needles or prisms. Melted sharply @ 147°C.

The batch from engine melted @ 149°C.

Mar. 7, 1916.

BSK.

Preparation of Di-phenyl-Guanidine from Diphenylcyanamide. (Carbodiphenylimide.)

$C_6H_5NH_2$ / $C_6H_5NH_2$ > C.S. + PbO → PbS + H_2O + C_6H_5N / C_6H_5N > C

(228) (223) (194)

(30) (30) (25)

30 g. S-carbanilide were dissolved in 250 cc. of pure benzol, 30 g. PbO added and the mixture heated on the water bath under a reflux for several hours. At end of this time the blackened PbO was filtered off, & ftd. several times with benzol, a second 30 g. portion of PbO added to filtrate, and boiling continued several hrs. longer. Then filtered, PbO ftd. with benzol and the benzol distilled from filtrate.

(X) The residue after distn. of benzol was a clear colored syrup (19 g.) which polymerized spontaneously to a white substance. Before this polymerization took place, however, an ether of NH_2 Aff was added and the mixture well stirred. 16 g. of the syrup was used for this & 3 g. left for further observation on polymerization.

Yield of carbodiphenylimide = 19.0 g = 76% Theory

X) — See next Pg.

4 — Reaction did not take place in desired manner. Then used ale. ammo with better results.

Nov. 21, 1914

Hoyt

Prepn. of Di-Ph-Guanidine (III.)
from
Diphenyl cyanamide.
(Carbodiphenylimide.)

Addition of NH_3 to
Diphenyl cyanamide —

Upon the ammonia(gas) could be added to the cyan., a partial polymerization of the latter was found to take place. After NH_3 had apparently not reacted with the diphenylcyanamid in 24 hrs., 24 cc. of alcoholic ammonia was added, with apparently little result. The resulting solid was then crystallized from alcohol fractionally and found in the main to be unchanged polymer & the cyan. supposed to be diphenyl-cyanamide, and melting therefore @ 157° C. (the same M.P. as obtained by the original boiling diphenylcyanamide on which a M.P. of ... after purification)

Another product melting @ 182-188° was also formed in lesser amount

ADK

Nov 10/37

On a cheap grey Tube for Special Brands.

Idea was to get a cheap grey tube that could be sold in competition with the British cheap tube. Tube would Horny.

	#62	#63	#63 Mod	
Smoked Rub	—	150	150	✓
Tube	300	150	150	✓
H.G.	100	100	100	✓
Brown Lub	40	40	40	✓
M.R.	40	40	40	✓
Spun Ox.	11	10	10	✓
Opaque Tube	21	30	30	—
Cellophane	29	30	30	—
# 40	2	2	2	?
Mannox R	35	1	—	
Paraffin	15	5	5	
Molyprene	—	1	3	✓
	546	537	550	

* Opaque - 2.0
* Highlite 02.

	#63	#63	#63 Mod
Burn	#1 Strip	5 Person	5 Person
A.A.	1.08	1.10	1.10
Rel. Hum.	52.57	52.59	52.8

#63 – Homeland will use some be #40 cure.
#63 Mod. – Called T.M.B.

Ex. No. G
U. S. Dist. Court.
S. D. of N. Y.
JAN 2

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Defendant's Exhibit T (Page 1)

MEMORANDUM SHIPPING ORDER

THE FALLS RUBBER COMPANY

ORDER NO. A_____

DATE BILLED_____

Form 1P

Ship to _____ Date _____

Address _____

Via _____

Terms 1

Bill to _____

E-G
8W-23

Quantity	Size	DESCRIPTION	Price	Discount	Extension
100	28 X 3	Grey Tube	x 6		
400	32 X 3½	"			
100	31 X 4		12		
400	33 X 4				
		(Price 50 % off list)			

9/4/17

Issued by _____ Approved _____

7168

SHIPPING ORDER

THE FALLS RUBBER COMPANY

CUYAHOGA FALLS, OHIO

No. A 12546

DATE Sept. 4, 1917

Customer's Order No. [illegible] Date of Customer's Order 9/4/17

SHIP TO Rubber City Clearing House,

BILL TO [illegible], O.

TERMS Credit

SHIP VIA	QUAN.	SIZE	DESCRIPTION	PRICE	SEP 13 1917 SHIPPED	AMOUNT	BALANCE	SEP 15 1917	
	100	28x3	Grey Tubes		0		100	27	73
	400	32-3½	" "		30		270	119	237
	100	31x4	" "		0		100	53	47
	400	3524	" "		46		254	115	239
							924		
			Less 50-5% Miller List						
			Hold						
			Clearance 28 Tubes						

Ex H
634-7

Defendant's Exhibit T (Page 2) 252

656

SHIPPING ORDER

THE FALLS RUBBER COMPANY

CUYAHOGA FALLS, OHIO

No. A 12840

DATE Sept. 20, 1917 SHIP TO Rubber City Clearing House,
Customer's Order No. Book Order - 18546 BILL TO Akron, O.
Date of Customer's Order

TERMS Cash

SHIP VIA To be called for

SEP 26 1917

QUAN.	SIZE	DESCRIPTION	PRICE	SHIPPED	AMOUNT	BALANCE
73	28x3	Troy Tubes	2 95	73		0
251	32x3½	" "	3 85	251		0
47	31x4	" "	4 85	47		0
239	33x4	" "	9 10	239		0
610						

Less 50-5% Miller last

OK

Def't Ex. No. 2
U. S. Dist. Court
N. D. of N. Y.
JAN 9 1918

0936

PHYSICAL TEST SHEET

Date 11/28/01 Observer [illegible]

Lab. Test No.	Number and Formula of Compound	Cure: Time Hrs	Cure: Time Min	Cure: Press Lbs	Dimensions of Test Piece: Thickness	Dimensions of Test Piece: Width	Breaking Strain: Pounds	Tensile Strength: Pounds per Square Inch	Tensile Strength: Average	Elongation: Actual	Elongation: % Original Length	Permanent Set: Actual	Permanent Set: % Original Length	Remarks
	T-63		30	50	2/64	3/64	34	1186.6	1268.0	7 1/2		4/32	12.5	
			↓	↓	2/64	4/64	40	1396.0		7 1/2		5/32	15.6	
					2/64	4/64	35	1221.5		7 1/2		5/32	15.6	
	T-63		45	50	2/64	4/64	40	1396.0	1630.3	7 1/2		4/32	12.5	
			↓	↓	2/64	4/64	50	1745.0		7 1/2		5/32	15.6	
					2/64	4/64	44	1535.6		7		5/32	15.6	
	T-63		60	50	2/64	4/64	44	1586.0	1691.2	9		5/32	15.6	
			↓	↓	2/64	4/64	56	1764.0		7 1/2		6/32	25.0	
					2/64	4/64	56	1612.4				6/32	18.75	

Ex. No. K
U. S. Dist. Court
S. D. of N. Y.
JAN 3 - 23

Defendant's Exhibit U

254

11/3/25 AC

Comp'd #63-B

Smoked sheet	150
Latex	150
H. G. Reclaim	100
Brown Substitute	40
Mineral Rubber	40
Zinc Oxide	10
Blanc Fixe	30
Sulphur	30
Carbon Black	2
Paraffin	5
Magnesium Oxide	1
	558

Compound No. 63 A

Date 10-12-25

Object of Test

Change Made

How Replaced

Tests: Thumb / Tooth / Puncture

Sp. Gr.

Ash

Compounded by

PHYSICAL TESTS DATA

Date of Test 10-12-25

CURE	TENSILE	~~FINAL~~ ELONG.	SET
Lighter.	1858	688	
Cream.	1845	725	
Av.	1852	707	

Remarks

Tested by J. F. McWhorter

J.F.M.
10-12-25

Comp'd 63A

Smoked sheet	150.
Latex	150.
H. G. Reclaim	100.
Brown Substitute	40.
Mineral Rubber	40.
Zinc Oxide	10.
Blanc Fixe	30.
Sulphur	30.
Carbon Black	2.
Paraffin	5.
Magnesium Oxide	1.
D.P.G.	0.2
	558.2

Compound No. 63 B

Date 10-12-25

Object of Test

Change Made

How Replaced

Tests: Thumb / Tooth / Puncture

Sp. Gr.

Ash %

Compounded by

PHYSICAL TESTS DATA

Date of Test 10-12-25

	CURE	TENSILE	~~FINAL LENGTH~~ Elong.	SET
	Lengthwise	1428	685	
	Crosswise	1426	720	
	Average	1427	703	

Remarks

Tested by J.F. McWhorter

Defendant's Exhibit X (Page 4)

259 **Defendant's Exhibit AA**

9

Defendant's Exhibit BB 260

9

261 **Defendant's Exhibit CC**

DIPHENYL
DIPHENYL
GUANIDINE
GUANIDINE

ACTION OF ORGANIC ACCEL.
ACTION OF ORGANIC ACCEL

DIPHENYL
DIPHENYL
GUANIDINE
GUANIDINE

N E N

263 **Defendant's Exhibit DD-1**

971

E. I. DU PONT DE NEMOURS & CO., INC.

Dyestuffs Department, Rubber Laboratory

Compound No. 486 Date Compd. 2/24/25 Date Tested 3/27/25 Date Reported 3/30/25

Formula

Smoked Sheet	50
Para Crepe	50
sulfur	3.5
Zinc Oxide	3.0
Dr calcined magnesia & Carbonate	0.75

SUMMARY OF PHYSICAL TEST DATA

Cure Minutes	Cure Temp	100%	200%	300%	400%	500%	600%	700%	800%	900%	Tensile Strength	Elongation at Break	Resistance to Tear
30	286°F					76					880	1010	
45	286°F					50					1360	980	
60	286°F					106					1410	970	
90	286°F					147					1850	950	

Remarks

Defts. Exhibit GG
Oct/25
mls

GG

Reported by E. I. Bridgwater

Defendant's Exhibit GG 264

972

Form 1960 21 - 31

DU PONT

E. I. DU PONT DE NEMOURS & CO., INC.

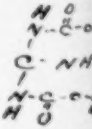
DYESTUFFS

Dyestuffs Department, Rubber Laboratory

Compound No. 519 Date Cured 9 12 25 Date Tested _____ Date Reported 9 12 25

Formula

Smoked Sheets	50
Amber Crepe	50
Zinc Oxide	3
Sulphur	3.5
Dicarbobenzyguanidine	0.75



SUMMARY OF PHYSICAL TEST DATA

CURE Minutes	CURE Temp	100%	200%	300%	400%	500%	600%	700%	800%	900%	Tensile Strength	Elongation at Break	Resilience by Ver
60	145°C				NO Cure								

Remarks

Defts' Exhibit H H
as of 1925
mfg.

Reported by E R Bridgwater

Defendant's Exhibit HH (Page 1)

DU PONT

E. I. DU PONT DE NEMOURS & CO., INC.

Dyestuffs Department, Rubber Laboratory

DU PONT DYESTUFFS

Record No. 522 Date Cured 9-15-25 Date Tested Date Reported 9-18-25

Smoked Sheets	50.	
Amb. Crepe	50.	
Zinc Oxide	3.	
Sulfur	3.5	C=NH
di benzoyl guanidine	0.75	N-C-O

SUMMARY OF PHYSICAL TEST DATA

Cure Hrs.	Cure Temp.	100%	200%	300%	400%	500%	600%	700%	800%	900%	Tensile Strength	Elongation at Break	Resistance to Tear
60	145°C				NO cure								

Reported by E. L. McQuaig

Defendant's Exhibit HH (Page 2) 266

974

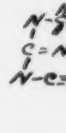
E. I. du Pont de Nemours & Co., Inc.

Dyestuffs Department, Rubber Laboratory

Compound No. 520 Date Compd. 7-15-25 Date Tested ——— Date Reported 9-15-25

Formula

Smoked Sheets	50	
Para Crepe	50	
Zinc Oxide	3	
Sulfur	3.5	
2 Hydroxymethyl 2 cyano guanidine	0.75	



SUMMARY OF PHYSICAL TEST DATA

CURE Minutes	CURE Temp.	100%	200%	300%	400%	500%	600%	700%	800%	900%	Tensile Strength	Elongation at Break	Resilience by Tor
60	145C				1/10.	Cure							

Remarks

HH

Reported by E R Mcguarke

Defendant's Exhibit HH (Page 3)

E. I. DU PONT DE NEMOURS & CO., INC.

Dyestuffs Department, Rubber Laboratory

Compound No. 526 Date Mixed 9-18-25 Date Tested _____ Date Reported 9-18-25

Formula

Smoked Sheets	50	
Amber Crepe	50	
Zinc Oxide	3	
Sulfur	3.5	
di-sulfo-Phenylguanidine	0.75	

SUMMARY OF PHYSICAL TEST DATA

CURE Minutes	CURE Temp.	100%	200%	300%	400%	500%	600%	700%	800%	900%	Tensile Strength	Elongation at Break	Resistance to Tear
60	141°C			NO CURE									

Remarks

HH

Reported by E. J. Midgley

976

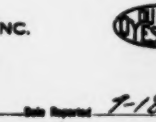
E. I. DU PONT DE NEMOURS & CO., INC.

Dyestuffs Department, Rubber Laboratory

Compound No. 525 Date Compd. 7-16-25 Date Tested _____ Date Reported 7-18-25

Formula

Smoked Sheets	50
Amber Crepe	50.
Zinc Oxide	3.
Sulfur	3.5
Di-thio. carbothoxyguanidine	0.75



SUMMARY OF PHYSICAL TEST DATA

CURE Minutes	CURE Temp.	100%	200%	300%	400%	500%	600%	700%	800%	900%	Tensile Strength	Elongation at Break	Resilience % Rec
60	141.5°C			110	cure								

Remarks

HH

Submitted by E R Bridgwater

Defendant's Exhibit HH (Page 5)

9317

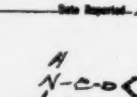
E. I. DU PONT DE NEMOURS & CO., INC.

Dyestuffs Department, Rubber Laboratory

Compound No. 523 Date Cured 7-16-25 Date Tested Date Reported 7-18-25

Formula

Smoked Sheets	50
Amber Crepe	50
Zinc Oxide	3
Sulfur	3.5
Di-nitro dibenzoyl guanidine	0.75



SUMMARY OF PHYSICAL TEST DATA

Cure Minutes	Cure Temp.	100%	200%	300%	400%	500%	600%	700%	800%	900%	Tensile Strength	Elongation at Break	Resistance to Tear
60	144 SR				NO cure								

Remarks

Reported by E. L. Bridgwater

978

DU PONT

E. I. du PONT de NEMOURS & Co., Inc.

Dyestuffs Department, Rubber Laboratory

DUPONT DYESTUFFS

99

Compound No. Ed 1 B Date Cured 9 11 25 Date Tested 9 11 25 Date Reported 9 11 25

Formula

Phila no 67 (C. Shedden)	70.
Brazil Crepe	5.
Lime	1.
sulfur	4.
Barytes	18.
tri-phenyl guanidine	2.

SUMMARY OF PHYSICAL TEST DATA

CURE Minutes	CURE Temp.	100%	200%	300%	400%	500%	600%	700%	800%	900%	Tensile Strength	Elongation at Break	Resilience % Rise
15	274°F										672	8.6"	
											854	9.6"	
											742	8.8"	
									average		756	9.0"	

Remarks

Reported by E R Bridgwater

Defendant's Exhibit II (Page 1)

979

DU PONT

E. I. DU PONT DE NEMOURS & CO., INC.

DU PONT DYESTUFFS

Dyestuffs Department, Rubber Laboratory

Compound No Ed-1 Date Cured 9-17-25 Date Tested 9-17-25 Date Reported 9-17-25

Formula

Phila. no 67 (C Stokely)	70.
Brown crepe	5.
Lime	1.
sulfur	4.
barytes	18.
di. thiocarbanilide	2.

SUMMARY OF PHYSICAL TEST DATA

Cure Minutes	Cure Temp	100%	200%	300%	400%	500%	600%	700%	800%	900%	Tensile Strength	Elongation at Break	Resistance to Tear
[redacted]													
45	274 F										657	7.6"	
											778	8.4"	
											702	7.6"	
									average		712	7.8"	

Remarks

Reported by E R Bridgwater

980

Form 1965 2M 9-24

DU PONT

E. I. DU PONT DE NEMOURS & CO., INC.

DUCO & DYESTUFFS

Dyestuffs Department, Rubber Laboratory

Compound No. E&L-A Date Cured 9-17-25 Date Tested 9-17-25 Date Reported 9-17-25

Formula

Phila No. 69 (C Shoddy)	70.
Brown crepe	5.
Lime	1.
sulfur	4.
barytes	18

SUMMARY OF PHYSICAL TEST DATA

CURE Minutes	CURE Temp.	100%	200%	300%	400%	500%	600%	700%	800%	900%	Tensile Strength	Elongation at Break	Residue in Tire
15'	274°F										585	9.2"	
											640	9.8"	
											765	9.9"	
									average		663	9.63"	

Remarks

II

Reported by E L McGavack

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Defendant's Exhibit II (Page 3)

E. I. DU PONT DE NEMOURS & CO., INC.

Dyestuffs Department, Rubber Laboratory

Compound No. Ed 2 B Date Cured 9-17-25 Date Tested 9-17-25 Date Reported 9-17-25

Remarks		
	Phila Lehigh (Yahoola)	68.
	Hydrolene	10.
	Turpentine	3.
	Fossil flour	12.
	Mroda	1.5
	Limo	225
	Sulfur	225
	tri-phenyl guanidine	1.0

Df 4 MM 10/15/25 NC.

SUMMARY OF PHYSICAL TEST DATA

CURE Minutes	CURE Temp.	100%	200%	300%	400%	500%	600%	700%	800%	900%	Tensile Strength	Elongation at Break	Resistance to Tear
20	274°F										728	240%	
											666	300%	
											705	300%	
								average			700	287%	

Remarks

Reported by E. R. McGwaker

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Defendant's Exhibit MM (Page 1)

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E. I. DU PONT DE NEMOURS & CO., INC.

Dyestuffs Department, Rubber Laboratory

Compound No. Ed 2 Date Cured 9-17-25 Date Tested 9-17-25 Date Reported 9 17 25

Formula

Phila Lehigh (Schaadly)	68.
Hydrolene	10.
Turpentine	3
Rosin Flour	17
Carb. Black #1 (Incorp.)	1.5
Lime	2.25
Sulphur	1.0

SUMMARY OF PHYSICAL TEST DATA

CURE Minutes	CURE Temp.	100%	200%	300%	400%	500%	600%	700%	800%	900%	Tensile Strength	Elongation at Break	Reaction to Ice
20	274°F										51.7	3.7	
											648	38	
											646	37	
								average			620	3.73	

Remarks

FMM

Reported by: E R Bridgwater

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Defendant's Exhibit MM (Page 2)

E. I. DU PONT DE NEMOURS & CO., INC.

Dyestuffs Department, Rubber Laboratory

Compound No. Ed 2-A Date Mixed 9-17-25 Date Tested 9-17-25 Date Reported 9-17-25

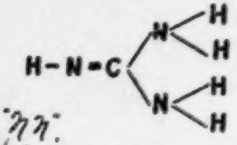
Basis Phila Lehigh (Schedly) 68.
Hydrocarbene 10.
turpentine 3.
Rosin flour 12.
Inverted Carbon black 1.5
lime 2.25
sulfur 2.25

SUMMARY OF PHYSICAL TEST DATA

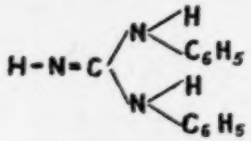
Cure Time	Cure Temp.	100%	200%	300%	400%	500%	600%	700%	800%	900%	Tensile Strength	Elongation at Break	Resilience by Tele
20	274°F										473	4.0"	
											505	4.2"	
											482	4.0"	
							average				487	4.07"	

Reported by E. K. Bridgwater

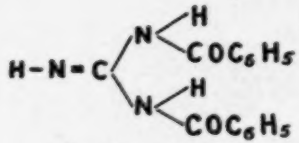
Defendant's Exhibit MM (Page 3)



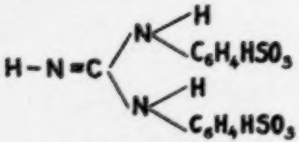
Guanidine



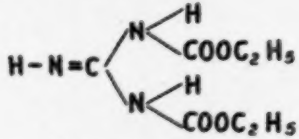
Diphenylguanidine



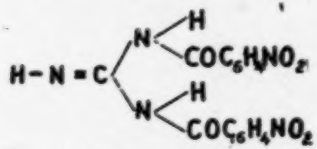
Dibenzoylguanidine



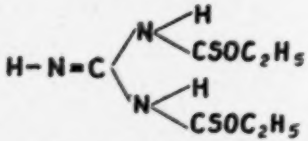
Disulphophenylguanidine



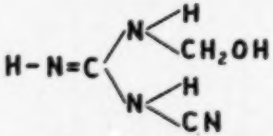
Dicarbethoxyguanidine



Dinitrodibenzoylguanidine



Dithiocarbethoxyguanidine



Hydroxymethylcyanoguanidine

C Represents Carbon N Represents Nitrogen H Represents Hydrogen S Represents Sulphur O Represents Oxygen.

C_6H_5 Represents Phenyl group COC_6H_5 Represents Benzoyl group $C_6H_4SO_3$ Represents Sulphophenyl group

$COOC_2H_5$ Represents Carbethoxy group $COC_6H_4NO_2$ Represents Nitrobenzoyl group

$CSOC_2H_5$ Represents Thiocarbethoxy group CH_2OH Represents Hydroxymethyl group C N Represents Cyano group

—(Lines) Represent "Valences" or bonds between atoms

Defendant's Exhibit NN

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UNITED STATES PATENT OFFICE.

FRITZ HOFMANN AND KURT GOTTLOB, OF ELBERFELD, GERMANY, ASSIGNORS TO SYNTHETIC PATENTS CO., INC., OF NEW YORK, N. Y., A CORPORATION OF NEW YORK.

VULCANIZATION OF RUBBER AND PRODUCTION OF VULCANIZED-RUBBER PRODUCTS.

1,126,469. Specification of Letters Patent. Patented Jan. 26, 1915.

No Drawing. Application filed October 16, 1913. Serial No. 795,506.

To all whom it may concern:

Be it known that we, FRITZ HOFMANN and KURT GOTTLOB, doctors of philosophy, chemists, citizens of the German Empire, residing at Elberfeld, Germany, have invented new and useful Improvements in Vulcanization of Rubber and Production of Vulcanized-Rubber Products, of which the following is a specification.

In the applications, Serial Nos. 688761 and 688762, filed April 5, 1912, there are described new caoutchouc substances and the vulcanization products thereof, which are obtained by treatment of the autopolymerization product of beta-gamma-dimethylerythrene with basic substances and by subsequent vulcanization of the resulting products.

In our companion application Serial No. 795,506, filed October 16, 1913, we have described that among these basic substances certain methylene bases, either open carbon chain or closed carbon chain bases, such as tetramethylenediamin, pentamethylenediamin, beta-beta-dimethyl-delta-methyltrimethyleneamin derivatives, and the urea and carbon bisulfid derivatives of bases such as dimethylamin, as well as piperidin, methylpiperidin, n-thiopiperidin, benzaldipiperyl, piperidyldithiocarbamidate or piperidin, monopiperidyl urea, and in particular the solid and liquid derivatives of piperidin and its homologues which have no odor and only a faint odor, lend themselves excellently for the production of vulcanization products from polymerized beta-gamma-dimethylerythrene, and particularly from the autopolymerization product of this hydrocarbon.

We have now discovered that the vulcanization of rubber generally, either natural or synthetic, can be materially promoted by the use of such a methylene base and particularly by the use of a piperidin base, etc.; and that by the use of such a base the vulcanization process proceeds more smoothly and more quickly while an improved product is obtained. The present invention is accordingly generic in its nature to the vulcanization of natural and synthetic rubbers.

According to the process of the present invention the rubber, either natural or synthetic, is treated either before or simultaneously with the addition of sulfur or of other vulcanizing agents with a methylene base and more specifically with a methylene base which is not fugitive at the temperature of vulcanization, and the base is thus incorporated within the mass and remains therein combined either physically or chemically. Among such bases may be mentioned the saturated aliphatic amins and their derivatives (both open carbon and closed carbon chain compounds) such as tetramethylenediamin, pentamethylenediamin etc. which are saturated methylene open carbon chain bases, beta-beta-dimethyl-delta-methyltrimethyleneimin and its urea derivatives, the urea and carbon bisulfid derivatives of such bases as dimethylamin, etc., the carbon bisulfid derivative of pyrrolidin (tetrahydropyrrol), and as particularly valuable bases there may be mentioned piperidin (hexahydropyridin), its derivatives and homologues, etc., such as methylpiperidin, n-thiopiperidin, benzaldipiperyl, pipiperidyldithiocarbamidate of piperidin, monopiperidyl urea, etc., and in particular those solid and liquid derivatives of piperidin and its homologues which have no odor, or only a faint odor.

The term methylene base is used as generic to those bases which are saturated bases as distinguished from unsaturated bases such as anilin or pyridin, and which are not fugitive at the vulcanization temperature, and this term is intended to include as a generic term non-fugitive open carbon chain bases and closed carbon chain imino bases such as piperidin, etc. By the use of these bases, and particularly by the use of piperidin the vulcanization not only proceeds more quickly and more smoothly, but it is also possible to obtain either an improved vulcanized soft or hard rubber product.

The rubber used in the present invention to form the vulcanized hard or soft rubber product may be either natural or synthetic. In certain respects the synthetic rubbers differ from the natural rubber and the vulcanization problems presented are in many cases peculiar to the synthetic rubbers. The synthetic rubber are normally free from such nitrogenous constituents and such resins as are normally present in natural rubber. Frequently also the synthetic rub-

Defendant's Exhibit NN

bers contain more or less of the dimeric hydrocarbons or polymerization products produced at the same time as the synthetic rubber, which are on the other hand absent in natural rubbers. The vulcanization process appears in many cases to be materially affected by the presence or absence of these heterogeneous substances, but the process of the present invention is nevertheless of general application in the vulcanization of natural rubber, and of synthetic rubbers obtained by the polymerization of rubber-yielding hydro-carbons, such as the butadiene series among which there may be mentioned isoprene, erythrene, beta-gamma-dimethyl-butadiene etc.

The following examples further illustrate the novel process and the production of the novel products according to the present invention:—

Example 1: 100 parts of Pará-rubber are mixed with 10 parts of sulfur and 0.5 parts of piperidin and heated for 15 minutes to 135–145° C. (3½ atmospheres). In this way a soft vulcanized product is obtained which contains 3.5 per cent. of combined sulfur. In the absence of piperidin the reaction requires about 1 hour. If Pará-rubber is substituted by synthetic rubber, corresponding results are obtained.

Example 2: 100 parts of Pará-rubber and 10 parts of sulfur and 1.5 parts of piperidin are heated at 120–125° C. (2½ atmospheres) for 1 hour. A well vulcanized product is obtained. Without piperidin Pará-rubber gives an unfinished mass of little value under the same conditions.

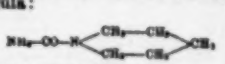
Example 3: 100 parts of erythrene caoutchouc, 10 parts of sulfur and 1 part of piperidin are heated at 120–125° C. (2½ atmospheres) for 20 minutes. A vulcanized erythrene caoutchouc is thus obtained.

Example 4: 100 parts of beta-gamma-dimethyl-butadiene rubber are heated with 10 parts of sulfur and 1 part of piperidin for 1 hour at 120–125° C. (2½ atmospheres). The result is a good soft rubber substance.

Example 5: 100 parts of beta-gamma-dimethyl-butadiene rubber are heated with 40 parts of sulfur and 0.75 parts of piperidin to about 155° C. (5–6 atmospheres). After 2 hours a hard rubber product is obtained which contains about 25 per cent. of combined sulfur. Without piperidin a product is obtained under the same conditions which contains only about 12 per cent. of combined sulfur.

Example 6: 100 parts of Pará-rubber, 10 parts of sulfur and 1 part of piperidyl-dithiocarbamidate of piperidin (melting at 173° C.) are heated for 15 minutes to 135–145° C. (3½ atmospheres). An excellent soft rubber substance is obtained. A good product is also obtained if the temperature is kept at 120–125° C. (2½ atmospheres) for about 1 hour. Similar or corresponding results are obtained with synthetic rubbers or when other natural rubbers are employed.

Example 7: 100 parts of beta-gamma-dimethyl-butadiene rubber, 50 parts of sulfur and 1 part of mono-piperidylurea of the formula:



are heated to 155° C. for 4 hours (5–6 atmospheres). An excellent hard rubber is obtained. If instead of 50 parts of sulfur only 10 parts are used, and it is heated to 120–125° C. (2½ atmospheres) for 1 hour, a soft rubber product is obtained. Other synthetic or natural caoutchoucs may be used in the above example; *e. g.* isoprene rubber, erythrene rubber, etc., also sodium butadiene rubber; also sodium isoprene rubber, etc.

The piperidin compounds mentioned in the above examples can be substituted by n-thiopiperidin (*Michaelis*, Berichte 28, 1013) or by benzalpiperyl (*Journal f. prakt. Chemie* (2), Band 36, p. 130) or by other solid or liquid derivatives of piperidin or its homologues.

Example 8: 100 parts of Pará-rubber, 10 parts of sulfur, and 1 part of the addition product of dimethylamin and bisulfid of carbon are heated for 15 minutes to 130–135° C. (3 atmospheres). A well vulcanized product is obtained. Without the above substance the reaction requires over 1 hour.

Example 9: 100 parts of beta-gamma-dimethylbutadiene rubber, 10 parts of sulfur, and 1 part of tetramethylenediamin are heated for 1 hour to 120–125° C. (2½ atmospheres). A soft rubber substance is obtained.

Example 10: 100 parts of Para-rubber, 100 parts of beta-gamma-dimethylbutadiene rubber, 20 parts of sulfur and 3 parts of the urea derivative of beta-beta-dimethyl-delta-methyl-trimethylenediamin are heated for 2 hours to 155° C. (5–6 atmospheres). An excellent hard rubber is obtained. Instead of the Pará-rubber and dimethylbutadiene rubbers, other synthetic rubbers or other natural rubbers may be employed.

In the above examples the addition of the piperidin and other methylene bases materially shortens the usual time required for vulcanization. If the process is continued for a longer time, a lower temperature may be employed, or if the process is continued at the usual temperature and time of vulcanization, a larger combination of sulfur is effected and a harder product is obtained. The results thus accomplished are much more marked than when other bases such as pyridin, quinolin, dimethylanilin are present. These bases hardly possess the

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property of accelerating and improving the vulcanization.

The vulcanized rubbers obtained according to the above examples contain the sulfur of vulcanization and a small amount of the added methylene base, combined therewith, either physically or chemically or in part physically and in part chemically.

We claim:

1. The process of producing a vulcanized rubber which comprises incorporating with rubber a small amount of a methylene base, and heating the resulting product with a vulcanizing agent to effect vulcanization.

2. The process of producing a vulcanized rubber which comprises incorporating with rubber a small amount of a heterocyclic methylene base, and heating the resulting product with a vulcanizing agent to effect vulcanization.

3. The process of producing a vulcanized rubber which comprises incorporating with rubber a small amount of a piperidin base, and heating the resulting product with a vulcanizing agent to effect vulcanization.

4. The process of producing a vulcanized rubber which comprises incorporating with rubber a small amount of piperidin, and heating the resulting product with a vulcanizing agent to effect vulcanization.

5. The process of producing a vulcanized rubber which comprises incorporating with natural rubber a small amount of a methylene base and heating the resulting product with a vulcanizing agent to effect vulcanization.

6. The process of producing a vulcanized rubber which comprises incorporating with natural rubber a small amount of a heterocyclic methylene base, and heating the resulting product with a vulcanizing agent to effect vulcanization.

7. The process of producing a vulcanized rubber which comprises incorporating with natural rubber a small amount of a piperidin base, and heating the resulting product with a vulcanizing agent to effect vulcanization.

8. The process of producing a vulcanized rubber which comprises incorporating with natural rubber a small amount of piperidin, and heating the resulting product with a vulcanizing agent to effect vulcanization.

9. As a new article of manufacture a vulcanized rubber combined before vulcanization with a small amount of a methylene base.

10. As a new article of manufacture a vulcanized rubber combined before vulcanization with a small amount of a heterocyclic methylene base.

11. As a new article of manufacture a vulcanized rubber combined before vulcanization with a small amount of a piperidin base.

12. As a new article of manufacture a vulcanized rubber combined before vulcanization with a small amount of piperidin.

13. As a new article of manufacture a vulcanized natural rubber combined before vulcanization with a small amount of methylene base not fugitive at the vulcanization temperature.

14. As a new article of manufacture a vulcanized natural rubber combined before vulcanization with a small amount of heterocyclic methylene base.

15. As a new article of manufacture a vulcanized natural rubber combined before vulcanization with a small amount of piperidin base.

16. As a new article of manufacture a vulcanized natural rubber combined before vulcanization with a small amount of piperidin.

In testimony whereof we have hereunto set our hands in the presence of two subscribing witnesses.

FRITZ HOFMANN. [L. S.]
KURT GOTTLOB. [L. S.]

Witnesses:
HELEN NUFER,
ALBERT NUFER.

Copies of this patent may be obtained for five cents each, by addressing the "Commissioner of Patents, Washington, D. C."

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VULCANIZATION ACCELERATORS.

BY S. J. PEACHEY.

[SPECIALLY CONTRIBUTED.]

In an article which appeared in a recent issue of THE INDIA-RUBBER JOURNAL as a reprint from the pages of *Metallurgical and Chemical Engineering*, Mr. A. H. King furnishes an interesting and instructive account of the present position of a comparatively new branch of rubber chemistry, viz., the employment of organic catalysts as accelerators of the vulcanizing process. The article referred to appears to be the first contribution on the subject to current English literature, and as for this reason it is likely to attract the attention of manufacturers to a highly important development in the rubber industry, the present writer feels that it is desirable to call attention to one or two important omissions from what is otherwise a most useful and exhaustive survey of the subject.

The author deals firstly with the well-known mineral accelerators, such as lime, magnesia, and litharge, and then proceeds to give a detailed account of the preparation and properties of the more recently discovered organic activators. The prototype of these is piperidine, the use of which as an accelerator was patented in Germany by Bayer and Co. in 1912. Other more or less effective agents were discovered a little later, and these receive due attention in Mr. King's article. Unfortunately the reader is left with the impression that the initiation and development of this branch of rubber research has been entirely due to the labours of German chemists.

It is quite true that in their efforts to bring about a satisfactory vulcanization of their so-called synthetic rubber (which in the strict chemical sense is not rubber at all) the Germans were led to the discovery of an agent which possesses the property of facilitating the union of rubber and rubber-like substances with sulphur, but it is equally true that by far the most satisfactory organic accelerator, judged from the manufacturer's point of view, was discovered in a British laboratory, and is now being made in a Manchester works, and employed regularly and successfully by some of the largest and best-known rubber firms in the country.

The substance referred to is known as accelerene, and consists essentially of paranitroso dimethylaniline (Eng. Pat. 4263/14). It is a compound wholly different in type from the German accelerators, in that it owes its activity to the presence of the nitroso group, and not to any feeble basic properties which it may possess. It is one of the most powerful vulcanization catalysts known; added to a rubber mixing in the proportion of one-third to one-half per cent. (0.3-0.5 per cent.) it reduces the time needed for vulcanization to *one-third* of the normal, and even this reduction does not represent the limit of its power, for if used in conjunction with certain other familiar substances a reduction to one-eighth of the normal time is readily obtained. The latter extreme reduction in the time of vulcanization is, however, not to be recommended, except in the case of quick repair compounds, but the reduction to one-third gives highly satisfactory results. Generally speaking, the best effects are obtained with medium and high-class mixings. Cheap mixings containing much reclaim or waste do not respond so readily to the catalytic action of the accelerator. In the case of mixings containing golden sulphide of antimony and little or no free sulphur it is noteworthy that the catalyst produces hardly any acceleration. In such cases a sufficient quantity of free sulphur must be added, and the percentage of antimony sulphide may then be reduced to that needed to p the desired colour to the mixing, after which the reduction in the time of vulcanization is attained.

In the manufacture of vulcanite the results obtain by the use of paranitroso dimethylaniline are very strik With the addition of 0.75 per cent. of the accelerato pure mixing of 100 parts of rubber and 40 parts of sulp may be fully vulcanized in two hours instead of the period of six, yielding a hard and very durable produc

Another point of considerable interest to manufacture is the fact that sulphuring-up may be completely p vented by the use of paranitroso dimethylaniline. order to obtain this effect, the amount of sulphur in mixing is reduced to something approaching the theore cal proportion required to yield the desired coefficient vulcanization. Thus, for example, the quantity of s phur employed may be reduced to as low a figure as to 3.5 per cent. The usual percentage (0.5) of the celerator is then added, and the mixing cured in ordinary manner. In such cases there is naturally li or no reduction in the time of vulcanization owing to diminished proportion of sulphur present. The power the catalyst is expended here in bringing about a pra cally complete combination between the molecules of rubber and of the sulphur, with the result that little o free sulphur remains in the rubber, and sulphuring becomes impossible.

Paranitroso dimethylaniline possesses one very import advantage over the other recently-discovered accelerato a fact which was first pointed out by certain firms w have tested different types of catalyst in works practi Whilst the German products undoubtedly produce a ra acceleration of the vulcanizing process, and are from t point of view quite satisfactory, they suffer from a seri drawback in that the vulcanization does not cease wh the goods are removed from the pan or the press, continues during storage, thus causing deteriorati Paranitroso dimethylaniline, on the other hand, produ an equally great acceleration, but shows no tende whatever to bring about after-vulcanization, even on p longed storage of the goods. The truth of this statem has been tested over a period of two years.

It appears also that goods vulcanized in presence of new accelerator show a somewhat greater tensile stren than those cured in the normal time. Investigations this point have not yet been completed, but a probab explanation is that the greatly reduced time of heat needed to bring about perfect vulcanization leads to diminished amount of depolymerisation, and this res in an increase in the nerve or strength of the rubber.

The above points are all of importance to the manufa turer, but the one which is likely to make the strong appeal is the fact that with the aid of these new celerators the output of an existing vulcanizing plant m be trebled at a comparatively small cost. It will probab be generally conceded that after a lapse of some thr quarters of a century a new principle has at last be introduced to the rubber industry.

The writer hopes that this brief article may suffice show manufacturers that not only in the production rubber goods does the Old Country hold its own, but i in original research on the chemistry and technology rubber it has now taken the lead.

Defendant's Exhibit "PP."

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Communication.

THE ACCELERATION OF VULCANISATION.

BY T. A. BRAZIER.

There methods are available for the speeding-up of the vulcanisation process: (1) raising the temperature, (2) increasing the proportion of sulphur relative to rubber, (3) introducing an accelerator.

Effect of temperature.

The effect of alteration of temperature is similar to that for other chemical reactions, the temperature coefficient being between 2 and 3 for 10° C. The suggestion has been made that some accelerators, lead oxide in particular, are not genuine catalysts, but that they merely react with part of the sulphur with evolution of heat, thereby raising the temperature of the reacting mass above that of the surrounding heating medium (Weil, Gummi-Zeit., 1911, 25, 710, 748). The insufficiency of this explanation is evident from the fact that such an effect should be almost negligible at the surface of the rubber in contact with the mould, whilst in the interior it would be marked; thick slabs also would vulcanise much more rapidly than thin sheets; both these consequences of the theory are contrary to experience. It is quite possible, however, that many vulcanisation accelerators do exert a slight thermal effect in addition to their purely catalytic influence.

The curves given in Fig. 1 represent results of some of our experiments as to the rate of vulcanisation at temperatures ranging from 130° C. (35 lb. steam pressure) to 160° C. (96 lb.) for a mixture of pale crêpe rubber (90) and sulphur (10); the corresponding curve for 125° C. will be found in Fig. 4. Pale crêpe rubber was chosen as showing greater uniformity in rate of vulcanisation than other forms of rubber, and was taken as far as possible from one raw. For the introduction of the sulphur a short mixing of sulphur with approximately an equal weight of rubber was used; the composition of this mixture was checked by analysis, and the correct proportion weighed out for mixing with the remainder of the rubber. In this way the almost inevitable loss of sulphur that during the customary method of mixing was avoided.

The progress of vulcanisation may be followed in at least three different ways: (a) by the combination of sulphur; (b) by the gradual decrease in the extensibility of the rubber at a definite load (or increase of the load necessary to produce a definite elongation); within the range of the experiments in this paper, this shows a roughly rectilinear relationship with the period of vulcanisation. Unfortunately, this method is influenced to a greater extent than either (a) or (c) by the mechanical treatment of the rubber during mixing and the subsequent milling operation. Increased working or heating having a tendency to exaggerate the extensibility figure. The approximation of the curve to a straight line and the close proximity of extensibility values for duplicate samples (see p. 136 T) are evidence of the considerable degree of accuracy attainable with careful working. For the purpose of comparison however different samples are stretched at 600% (doubling the original length) at a load of 0·5 kilo. per sq. cm. has been arbitrarily assumed as a standard dependent upon this paper; (c) by the time required to produce maximum tensile strength.

The last method, although of less importance than might be expected in technical practice, is of considerable value in experimental work as supplying a convenient and rapid method for comparing rates of vulcanisation, e.g., of different rubbers or at different temperatures, the maximum tensile strength determined within three days of vulcanisation, being observed with a product containing approximately 5 of combined sulphur calculated on the rubber. The actual value of the breaking strength of a rubber test piece is always more or less fortuitous; however, as vulcanisation beyond the condition necessary for the attainment of the maximum strength causes a very rapid weakening, the position of the maximum is relatively easily determined. The peaked curves in Fig. 1 indicate the position of the maximum rather than the actual magnitude of the values.

It will be observed that the temperature coefficient manifests no tendency to any regular increase or decrease with rise of temperature, the mean value calculated by all three methods of comparison) from the figures represented in the curves for the rubber-sulphur mixture at 120° to 160° C. approximating to 2·2. This appears to indicate that the alteration forms ordinarily present in molten sulphur to relative proportions dependent on the temperature, must possess equal or at least comparable vulcanising activity (see Trans. Annual Report, 1919, 4, p. 325).

The extent to which the vulcanisation period in technical work can be lessened by raising the temperature is limited by various considerations, not the least of which is the poor thermal conductivity of rubber and the consequent danger of unequal heating, involving local irregularities in the degree of vulcanisation.

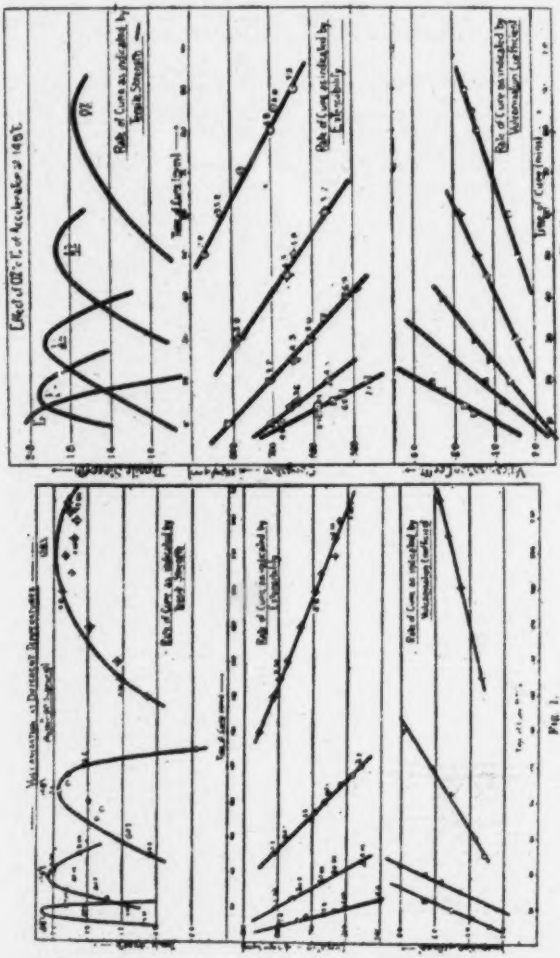
Increase of proportion of sulphur.

Many old compounding ingredients and specifics of the rubber trade, often bearing fanciful names, contained—undeclared—considerable proportions of free sulphur, mixtures of sulphur with various waxes and also with antimony sulphide may be quoted as better class examples. As the rate of vulcanisation of rubber-sulphur mixings containing less than, roughly, 10 of free sulphur is directly proportional to the percentage of free sulphur, the effect of such additional sulphur-containing ingredients on the rate of vulcanisation is obvious, and to-day is commonly realised.

For experimental work on the relative rates of vulcanisation of different rubbers or on the effect of various catalysts, the selection of a mixture of rubber and sulphur containing as much as 10% of the latter is advisable, not only because this quantity is more than sufficient to permit the progress of the change to well beyond the characteristic maximum strength, but also because it is sufficiently high to reduce to extent any disturbance arising from slight inaccuracies in the proportion of sulphur present. The possibility must always be borne in mind, however, that the activity of an accelerator may possibly be influenced by the proportion of free sulphur simultaneously present.

Use of a catalyst.

Almost all basic substances can act as catalysts to the vulcanisation process, e.g., magnesium oxide, lead oxide, lime, sodium hydroxide, potassium hydroxide, and also substances such as sodium amide, potassium glycerosside and sodium phenoxide, which, by interaction with the traces of water invariably present in rubber, are able to give rise to alkalis or bases. Typical examples of organic accelerators are piperidine, quinoline (the crude alkaloid mixture known as "quinoline" is commonly used), aniline, naphthylamine, p-phenylenediamine, hexamethylenetetramine, dimethylaniline, p-nitrosodimethylaniline, diphenylguanidine, aldehyde-ammonia, and simple carbon bisulphide or



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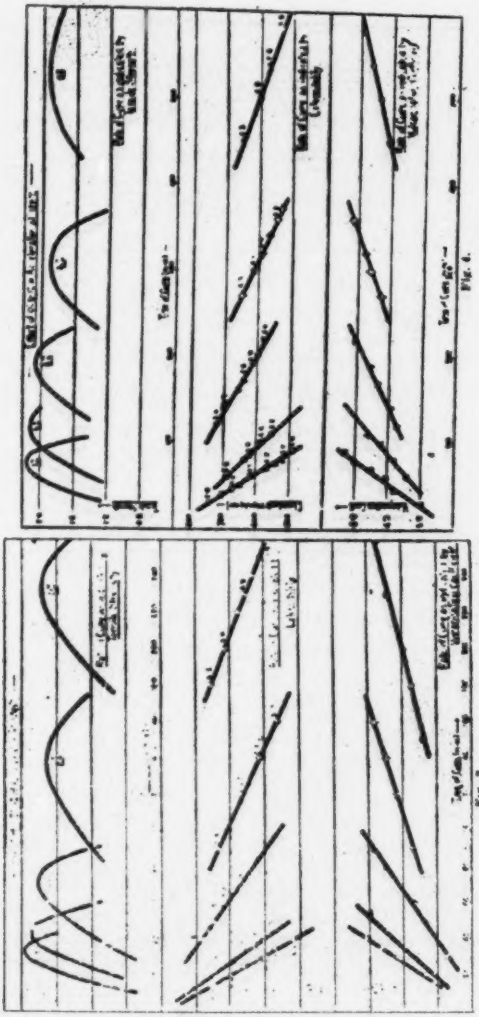

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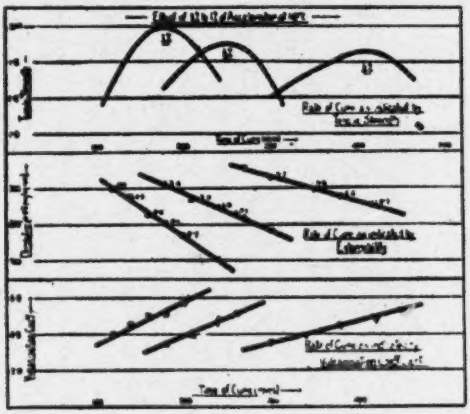

Fig. 5.

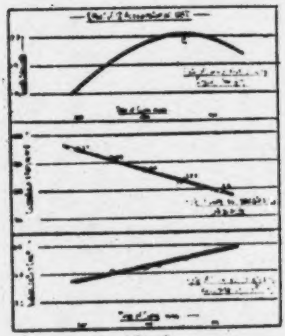

Fig. 6.

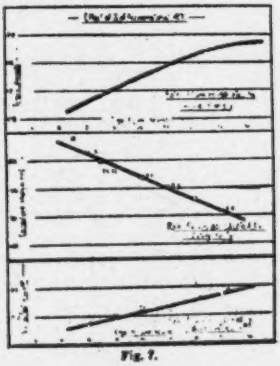

Fig. 7.

carbon dioxide derivatives of the amines, such as dimethylammonium dimethylcarbamate, the corresponding dimethyldithiocarbamate and thiocarbanilide. Compounds containing a nitro-group substituted into an aromatic cyclic nucleus are also effective catalysts, the best known example being *p*-nitrosodimethylaniline. Clearly there is a wide range of possible accelerators of these vermeer-

types.* In this connection there must also be mentioned the pre-vulcanized forming catalysts in rubber during its production. If the wet rubber

* The presence of nitrogen in all these organic substances of the connection with the detection by rubber. The nitrogen contained in a comparable extent with pure latex substances on producing vulcanization with sulphur and the extract subsequently did show an abnormally high percentage of nitrogen.

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ties, frankly complained from the loss, is kept for several days before being rolled and crushed, partial decomposition of the nitrogenous constituents of the retained serum sets in with the formation of organic bases. These are not eliminated by the subsequent rolling and washing, so that the resulting rubber exhibits exceptionally rapid vulcanisation.

As is illustrated clearly by our results in Fig. 1, the curve representing the rate of combination of rubber and sulphur does not follow the course expected from a simple chemical reaction, but, with less than 10% of free sulphur, is approximately rectilinear until the almost complete exhaustion of the sulphur (Spence and Young, this J., 1911, 817; 1912, 81, 785). This is probably to be explained by the occurrence of supersaturation; with mixtures of rubber and sulphur containing more than 10% of the latter, the progress of the fixation of sulphur follows the sinuous S course, which is commonly regarded as characteristic of an autocatalytic process (Skelton, Rubber Industry, 1911, 1-7; van Iterson, Comm. Netherlands Govt. Lab. for Advising Rubber Trade, 1910, 7-27). In the presence of an artificial catalyst, therefore, the compensation relation between the effect of the disappearance of sulphur and the extent of the increasing catalytic effect may be disturbed, so that the fixation of sulphur no longer follows a rectilinear course (van Iterson, *loc. cit.*).

Although the results as to the rate of vulcanisation of a simple sulphur mixing, as derived by these three methods, are comparable, in the presence of an extraneous catalyst, this is not necessarily so. The chemical action of sulphur on the rubber induces the physical alterations which constitute the advantage to be gained by vulcanisation, but the chemical and physical processes are not necessarily strictly proportionate, and some "accelerators" influence one more than the other. In the presence of certain accelerators the physical or mechanical alteration is disproportionately rapid, and the tensile strength attains its maximum" at a coefficient of vulcanisation (combd. sulphur × 100 ÷ rubber) well below the normal value of 5 (see p. 1207).

Other accelerators, on the other hand, reduce the sharpness of the optimum, so that the peak of the curve is less pronounced. In art other cases the catalyst may give rise to a vulcanised rubber with an abnormal extensibility relative to its coefficient of vulcanisation. Most of them, but not all, by reducing the time of heating necessary, cause the production of a rubber with a higher tensile strength than would be obtained by mere cold rub mixation at the same temperature without the catalyst, and in this direction reduction of the time of vulcanisation by using an increased percentage of sulphur can have a similar effect (van Iterson, *loc. cit.*, p. 200).

The effectiveness of one of the above-named organic catalysts, viz., aldehyde-ammonia, is demonstrated by the accompanying curves (Figs. 2-6) representing the results of experiments made, like those given in the earlier curves, with a mixture of pale crepe and sulphur (30 : 10), at various temperatures from 134° C. (at 35 lb. steam pressure) downwards, to an oil bath subsequently. Even at a concentration of 1 : 100 the effect is still exceedingly active, with 1% vulcanisation occurs so readily as to be possible in a reasonable period at 120° C., or less than 5 lb. steam pressure, Fig. 7, indeed, records the progress of vulcanisation at 98° C. It will be seen that the *temperature coefficient* calculated by the ratio of the speed of reaction at intervals of 10° C. from 106° to 146° is *practically the same as for the reaction in the absence of an artificial catalyst* (p. 1259), the average value for the accelerated mixings represented in Figs. 2-6 being 2·6. This observation militates against the belief of some investigators in this field that vulcanisation catalysts are not themselves able to expedite vulcanisation, but that during the early stages of the process they combine with sulphur, giving rise to substances which possess the desired activity. This view may be correct in certain cases, but evidently cannot be accepted generally for all vulcanisation catalysts. The average values of the coefficient with the various proportions of accelerator are given in the table:—

Average Temperature Coefficient.

Proportion of accelerator.	15 (100 : 667 C.)	17½ (100 : 570 C.)	20 (100 : 500 C.)	25 (100 : 400 C.)	33 (100 : 303 C.)
Method of taking—					
(a) Combination with sulphur	2·6	2·6	2·6	2·6	2·6
(b) Elongation at 0·5 kilo. per sq. mm.	2·6	2·5	2·5	2·4	2·1
(c) Maximum tensile strength	2·5	2·5	2·4	2·3	2·0

It is a striking fact that although the individual values of the temperature coefficient between 106° and 146° C. without exception oscillate closely about the mean value of 2·6, the interval 96°–106° C. shows a much greater value exceeding 5·0. This is doubtless due to the melting of the sulphur between these two latter temperatures, the normal melting point being lowered under the obtaining conditions. This observation supplies a confirmation of the statement on page 1257 as to the comparable effectiveness of the various allotropic forms.

The fact observed above, that the temperature coefficient possesses comparable values for mixings with and without an artificial catalyst, appears from other results in our possession to be a general one for all catalysts. This facilitates the representation of the relative effectiveness of different catalysts by means of a numerical factor. A factor representing the ratio of the respective periods of vulcanisation required for the attainment of a definite state of vulcanisation in a rubber-sulphur mixing, with and without a definite proportion of accelerator, will be independent of the temperature, it will be essential that this comparison be made at a stage of the vulcanisation process when the mixture still contains a considerable proportion of uncombined sulphur. The resulting "acceleration factor" may differ according to which of the three possible criteria—percentage of combined sulphur, maximum tensile strength and extensibility at definite load—is taken as fixing a definite state of vulcanisation. In the case of the accelerator used in the experiments now quoted the behaviour may be described as normal, all three methods giving comparable results. The effectiveness calculated in this way for the accelerator at various concentrations and at different temperatures is given in the following table; the figures in each case represent the mean of the values obtained by the three different methods of the comparison of rate of vulcanisation.

Mixings with rates, the proportions of 5, 4, 3, and 2 per-centiles of the accelerator increase the rate of vulcanisation at any temperature vulcanising temperature to 1·7, 2, 3, and 7½ times the normal. A

Defendant's Exhibit RR (Page 5)

"Acceleration factor."

Percentage	½	1	1½	2
Temperature:				
130°–140° C.	37	56	51	75
135°–145° C.	37	56	54	74
140°–150° C.	37	50	60	71

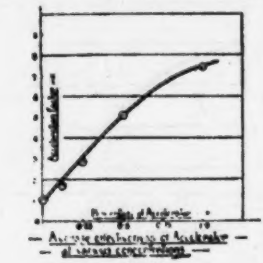


Fig. 8.

Fig. 8. The slight divergency (from the course of the smooth curve) of the points for the lower percentages is doubtless due to the relatively greater effect of the inevitable small loss of accelerator by vaporisation during the mixing operation.

Fig. 9 includes curves showing the relative effectiveness of isomeric substances, viz., *m*- and *p*-phenylenediamine as accelerators. The meta-compound is notably less active than its para-isomeride. It is of interest to note that the effectiveness of these two substances towards vulcanisation falls in the same order as their affinity constants as determined by Brodie in 1851. The low value of the coefficient of vulcanisation at the maximum tensile strength of the *p*-phenylene-diamine mixing will also be noticed. The absence of points on the extensibility curve beyond a co-efficient of 4 is due to the samples concerned being over-vulcanised and too weak for the test.

In Fig. 10 are given the results of tests on four different occasions and with three separate mixings, containing 1% of *m*-phenylenediamine; they are of importance, particularly in the extensibility section, as demonstrating the comparableness of figures obtained, even in independent experiments, with the standardised conditions adopted in this investigation.* The "acceleration factor" for *m*-phenylenediamine, calculated from the results in Fig. 8 has a mean value of approximately 1·5; for *p*-phenylenediamine judged by the physical methods the factor is approximately 3·3, whereas the rate of combination with sulphur indicates a value of only 3·0.

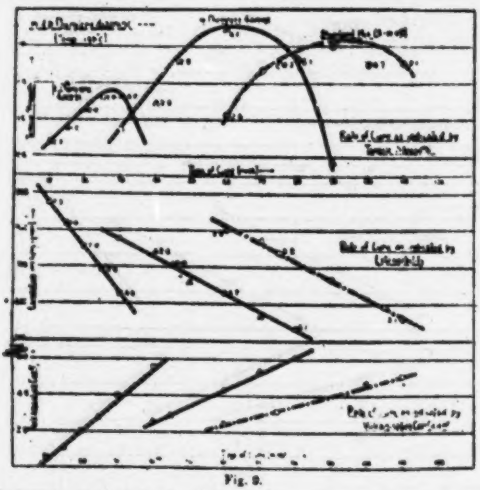
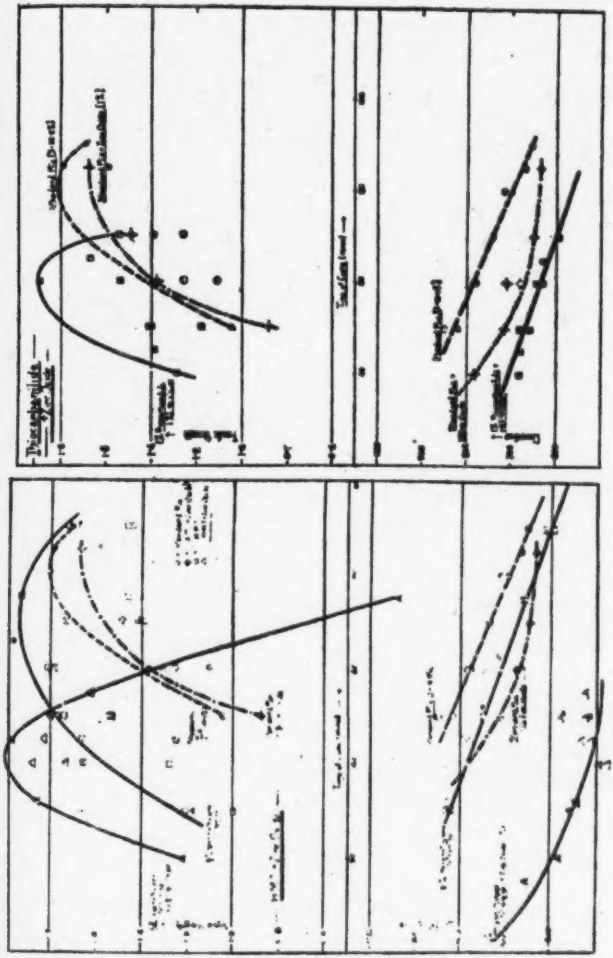


Fig. 9.

graphic representation of this result as to the relation between the proportion of the accelerator in question and the effect produced is given in

* In these and the previous experiments vulcanisation was effected by immersing the mixed rubber, enclosed in suitable moulds, in oil at the required constant temperature.



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Mixed Catalysts.

The effectiveness of a mixture of catalysts in an ordinary chemical reaction is well known not to coincide invariably with the sum of the effects produced by each independently. This peculiarity is also observable with vulcanisation catalysts (Heinze, *Gummi-Zeit.*, 1913, **28**, 120). Lead oxide with magnesium oxide, and β-naphthylamine-hydrochloride with another of one of its homologues, are cases which have already been quoted in the literature.

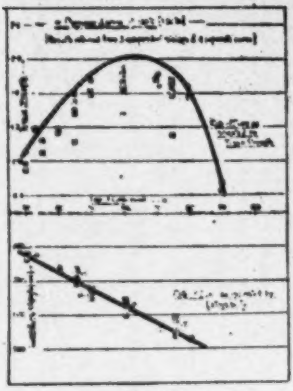


Fig. 10.

A related phenomenon probably is also the power of zinc oxide, which alone does not work rubber vulcanisation, to increase considerably the effectiveness of other organic catalysts such as hexamethylenetetramine and thiocarbanilide (see Figs. 11 and 12). As the latter by itself is practically inert, we have the interesting case of a mixture of two inactive substances exerting a distinct accelerating effect. In other cases we have found two vulcanisation catalysts to be "incompatible" in the sense that the effectiveness of the more active catalyst is actually decreased by the presence of the other.

As has been intimated already, an acceptable general explanation is not possible as to the mode of action of vulcanisation catalysts. In addition to the theories already mentioned, others have also been proposed. An observation of considerable interest in this connection is that rubber in solution or wetted with benzene becomes vulcanised by successive treatment with sulphur dioxide and hydrogen sulphide at the ordinary temperature (Peachey, this J., 1918, 696a). This reaction appears to be very suggestive in connection with the action of vulcanisation catalysts. None of the three modifications, Sλ, Sμ, and Sσ present in liquid sulphur appears to be in possession of exceptional chemical activity towards rubber (see above), but there is evidently a possibility that there is capable of existence yet another form of sulphur of much greater vulcanising power. Such a view, needing considerable modification however, has already been tendered (Indian-rubber World, 1919, **59**, 75; 1919, **59**, 214), but the scope for investigation in this direction is enormous. Indeed, the evidence available as yet is insufficient even to exclude the possibility that vulcanisation accelerators may activate the rubber and not the sulphur.

We are pleased to acknowledge the valuable assistance of Mr. C. W. H. Hoare, B.Sc., in connection with the experimental work recorded above, and our indebtedness to the Dunlop Rubber Co., in particular to Mr. J. V. Worthington, Technical Superintendent and Director, for permission to publish this paper.

DEFENDANT'S EXHIBIT "SS"

Comparison of Diphenylguanidine and Triphenylguanidine Formula of The Weiss Patent

	#1 (1359)	#2 (1375)
Rubber	50	50
Zinc Oxide	45.5	45.5
Sulfur	3.5	3.5
D. P. G.	1	....
T. P. G.	....	8

Time of cure, 40 lbs. steam	Tensile, lbs. sq. in.	Elongation, per cent	Tensile, lbs. sq. in.	Elongation, per cent
10	2390	640	2245	660
20	3410	635	3010	660
30	3480	590	3180	640
40	3470	570	3479	645
50	2460	470	3350	610

Test made Oct 5, 1925

E. W. Fuller.

Oct 13, 1925.

DEFENDANT'S EXHIBIT "UU"

UNITED STATES DISTRICT COURT, SOUTHERN DISTRICT OF NEW YORK

In Equity. No. —

DOVAN CHEMICAL CORPORATION, Plaintiff,

vs.

NATIONAL ANILINE & CHEMICAL CO., INC., Defendant

On Patent No. 1,411,231, to M. L. Weiss

Reply Affidavit of Monroe H. Daniels

STATE OF NEW YORK,
County of New York, ss:

Monroe H. Daniels, being sworn, deposes and says as follows:

I am of mature age and reside at 305 Sheridan Avenue, Newcastle, Pa. I am at present Production Superintendent of the Newcastle plant of the Seiberling Rubber Company.

I am the Monroe H. Daniels who executed an affidavit on or about February 25, 1922 in connection with the application for a patent of Morris L. Weiss, serial number 514727, filed November 12, 1921, for vulcanization accelerators.

From May, 1913, until about the middle of March, 1920, I was employed as an analytical chemist by the Republic Rubber Company at Youngstown, Ohio, and during the years 1917, 1918, 1919 and 1920 I was employed as Chief Chemist of said Republic Rubber Company. On or about October 18, 1917, I personally employed Morris L. Weiss as an analytical chemist for said Republic Rubber Company which employment continued until about the 15th of March, 1920. On or about October 7, 1918, I employed Corl H. Eaton as an analytical chemist for the Republic Rubber Company, and said Eaton remained with said company after my leaving them. Shortly after Weiss' employment with the Republic Rubber Company he was placed in charge of the analytical work, and was permitted to investigate certain problems relating to the chemistry of rubber including the analysis and testing of accelerators for vulcanization, which latter work was carried on during his spare time from routine work.

At my request said Weiss visited Pittsburgh, Pennsylvania, during the first week in January, 1919, in order to look up data relating to the production of organic compounds which could be used as accelerators. We had previously been particularly interested in and desirous of producing tri-phenylguanidine which had been to some extent previously used experimentally as an accelerator by us. Said Weiss had told me prior to his trip to Pittsburgh, Pa., that he had been working on di-phenylguanidine as an accelerator and that he had found it to be more powerful than tri-phenylguanidine.

Upon said Weiss' return from Pittsburgh, Pa. I instructed him to devote as much time as possible on triphenlyguanidine as that substance was the one in which I was most interested at that time although I consented to further investigation of di-phenylguanidine as an accelerator.

During the years 1918 and 1919 record books of experiments and compounding tests on rubber were kept in the laboratory, and these were known as laboratory X books. One of these books containing numbers from 1700 up to 1800 or more was kept personally by me, and another X laboratory book containing numbers from 2000 up to 2187 was kept in the laboratory of which Mr. Weiss had charge.

I attach hereto photographic copies of one page of the laboratory X book kept by me, said page being numbered "1777" which contains an entry made by me early in the year 1919 in which entry I recorded a compound to be used as a splicing cement for red inner tubes for automobile tires. The 10⅝ parts of di-phenylguanidine shown on this page, number 1777, was obtained from a quantity of that substance previously produced by Morris L. Weiss, and was mixed in the compound with the other ingredients indicated by William Halliday who did the compounding work and operated the experimental mixing mill. This cement proved to be very satisfactory and I decided to use the same as a standard compound in production as soon as diphenylguanidine should be produced in commercial quantities.

The copy of the page above referred to is marked "Daniels' Exhibit A."

I also attach to this affidavit three photographic copies of pages numbered "2006", "2034" and "2042" of the laboratory X book kept in the laboratory of which said Weiss had charge at that time. I have personally compared these photographic copies with the corresponding pages in the original record book at the Republic Rubber Company which comparison was made yesterday, June 9, 1922. The sheet previously referred to as "Daniels Exhibit A" was also similarly compared by me with the original on the same date. All of the handwriting on said sheets numbered 2006, 2034 and 2042 I recognize as being that of Morris L. Weiss and to the best of my knowledge and belief said entries were made in the regular course of business on or about the dates stated thereon as indicated by the figures at the bottom of the various vertical columns. Said last-mentioned sheets are marked as "Daniels' Exhibit B."

I note at the bottom of sheet No. 2006 that the margin has not been included in the photograph, but this sheet corresponds to the photostat copy of the same attached to the affidavit of Corl H. Eaton executed June 3, 1922, which includes the words "Compare with X 2005 H" which existed on the original page and which I have added in ink on the photographic copy produced by me, said words and figures also having been in said Weiss' handwriting on the original sheet.

I have read the affidavits of Corl H. Eaton executed June 3, 1922 and of Carl H. Zieme executed June 3, 1922 in this cause. I believe that the statements made by said Corl H. Eaton are in many respects untrue and misleading for the following reasons:

When said Eaton was first employed in October, 1918, by the Republic Rubber Company as an analytical chemist, he handled practically all of the routine analytical work as an assistant to Morris L. Weiss, and his duties were distinctly routine and not experimental. If he at any time did any work with tri-phenylguanidine such work did not begin until after the middle of the year 1919, and I personally have no knowledge of his working to any extent whatever on either tri-phenylguanidine or di-phenylguanidine which knowledge would naturally have come to me in the regular course of his laboratory work if the same had been included therein, and such work if done by said Eaton would have been recorded in the laboratory X book. It is true that Mr. Zieme is a graduate chemist but at that time, in the latter part of 1918, his relations with the Republic Rubber Company were emphatically not chemical in any way, shape or form. He was manager of the hose departments. As such he had charge of production only, and while he had a good knowledge of compounding due to his having been previously compounding chemist for the hose departments, he was out of touch with laboratory development and work. As a matter of fact his duties kept him in the plant practically all day. The time he spent in the laboratory was very short and usually in consultation with me or the man who had charge of compounding for the hose departments. Said Zieme had never stated to me that said Eaton had disclosed to him any proposal to use di-phenyl-

guanidine as a rubber accelerator which would have been the natural thing for him to do owing to his general interest in the advancement of the work of the plant and in view of my position as chief chemist. In view of the short time elapsing between said Eaton's employment by the Republic Rubber Company and the alleged date of the disclosure by Eaton to Zieme, it is improbable that they became well enough acquainted with each other so that said Eaton would have disclosed any personal ideas he may have had to said Zieme.

I have examined the original copy of a report now in the possession of Morris L. Weiss and drawn up by him in March, 1920, and recognize this report as being identical with a copy which was given to me by said Weiss about the 1st of March, 1920, which copy was left in the files of the Republic Rubber Company. This report was prepared by Mr. Weiss at my request due to the fact that the preliminary experimental work had shown that di-phenylguanidine was worth while producing in commercial quanities for use in the factory and I decided to use that report as a basis for making di-phenylguanidine on a large scale. This report covers the work done by Mr. Weiss during the period from the early part of 1919 until the date that the report was submitted to me about March 1, 1920.

It is true as stated by said Eaton in his affidavit that I attended the meeting of the American Chemical Society early in September, 1919, and heard the paper prepared by Kratz, Flower and Coolidge relating to rubber accelerators, However, I have no recollection of having had any conversation whatever about said paper with said Eaton and could not have made the statement alleged by said Eaton because of the fact that I had full knowledge that said Weiss had previously done considerable work on di-phenylguanidine and was much interested in that substance as an accelerator.

I did, however, upon my return from Philadelphia immediately tell Mr. Weiss that the statements made in the paper read by said Kratz confirmed our experience with diphenylguanidine as an accelerator and that we should continue the work on the substance and develop a commercial process if possible.

Regarding the statement made by said Eaton that he actually used di-phenylguanidine as a rubber accelerator during the month of January, 1919, and at various times thereafter, I cannot see how it would have been possible for him to have done such work in the chemical laboratory or in the factory without my knowledge and consent. It could not have been done by said Eaton as a part of his regular duties as he was engaged entirely in routine analytical work during the period that he alleges to have used diphenylguanidine. I do not believe that it is true that said Eaton suggested to said Weiss that diphenylguanidine would be a better accelerator than triphenylguanidine because of my knowledge of Weiss' earlier work on accelerators, which began soon after said Weiss' employment by the Republic Rubber Company in October, 1917.

Monroe H. Daniels.

Subscribed and sworn to before me this 10th day of June, 1922. Joe C. Thomson, Notary Public, etc. (Seal.)

(Here follow Defendant's Exhibits QQ and QQ-1, marked Side folio pages 297, 297½, 298, and 299)

DEFENDANT'S EXHIBIT "WW"

STATE OF MARYLAND,
Allegany County, To wit:

Before me, a Notary Public of the above mentioned State and County, personally appeared Clinton A. Carlton, who being duly sworn, deposes and says:

I was employed in June, 1917, as a Research Chemist by the Republic Rubber Company at Youngstown, Ohio, and left their employ early in the year of 1918, probably in March, the exact date, I do not remember.

Morris L. Weiss came into the employ of the Republic Rubber Company several months prior to my leaving and worked directly under my supervision.

UNITED STATES PATENT OFFICE.

MORRIS L. WEISS, OF BROOKLYN, NEW YORK, ASSIGNOR TO DOVAN CHEMICAL CORPORATION, OF WILMINGTON, DELAWARE, A CORPORATION OF DELAWARE.

PROCESS OF MAKING DIPHENYLGUANIDINE.

1,422,506. Specification of Letters Patent. Patented July 11, 1922.

No Drawing. Application filed July 2, 1921. Serial No. 482,143.

To all whom it may concern:

Be it known that I, MORRIS L. WEISS, a citizen of the United States, residing in the borough of Brooklyn, county of Kings, city and State of New York, have invented certain new and useful Improvements in Processes of Making Diphenylguanidine, of which the following is a full, clear, concise, and exact description.

Diphenylguanidine is indicated by the formula

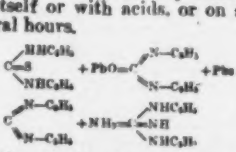
The object of my invention is the production of this substance in large or commercial quantities so that the same may be available in the chemical industries and particularly as an accelerator in the vulcanization of rubber compounds, as set forth in my co-pending application Serial No. 514,727, filed November 12, 1921, for vulcanization accelerators.

Prior to my invention it has not been possible to produce diphenylguanidine except in small quantities for use in chemical research and laboratory experiments. Even when produced for this purpose the product has been accompanied by the formation of comparatively large quantities of carbodiphenylimide, a thick treacle-like fluid, from which the diphenylguanidine is difficult to separate and which greatly reduces the yield of the latter.

Substituted guanidine was probably first synthetically produced in 1848 by A. W. Hoffman (Ann. Chem.-Parm 67,—129). Dry cyanogen chloride gas was passed into anhydrous aniline, from which he obtained the hydrochloride of a base which he termed "melaniline," at that time.

In 1869, Hoffman (Ber. 11,—460) synthesized diphenylguanidine by an entirely different method from that previously used. Thiocarbanilide was desulphurized with lead oxide in a solution of alcoholic ammonia. The resulting product had the same properties as that of his first product except that its melting point was 147° C. instead of 120°–130° C.

By Hoffman's last method, a large quantity of polymerized carbodiphenylimide is produced, due to the volatility of the ammonia, and so reduces the yield of diphenylguanidine that it is not possible to produce the chemical commercially. The very high volatility of the ammonia at the temperature of the reaction also results in a large loss. Schall has shown (Ber. 27,—2696) that carbodiphenylimide has a tendency to polymerize into three different isomeric forms. This may be accomplished by either digesting by itself or with acids, or on standing for several hours.



Carbodiphenylimide being very unstable, changes into isomeric forms before the combination with ammonia takes place. The longer the combination is delayed the more of the isomers are produced. The isomers do not combine with ammonia to form diphenylguanidine.

Weith (Ber. VII. 10—16) who first produced carbodiphenylimide or desulphurized diphenylthiourea

has shown that it combines with ammonia probably to form diphenylguanidine and that it is polymerized to form carbodiphenylimide. It also combines with water to form diphenylurea. By taking advantage of these suggestions and using an alcohol-water solution and by substituting an ammonium salt such as ammonium nitrate, sulphate, or chloride, which are not volatile at the reaction temperature 65°–70° C., I am enabled to minimize to a large extent the production of polymerized carbodiphenylimide, which otherwise forms due to the volatility of the ammonia, and thereby obtain a larger yield of diphenylguanidine.

I also found that the percentage of concentration of the alcohol and water solvent had an important effect on the reaction.

One form of the process, which I at present deem preferable, may therefore be described as follows:

Thiocarbanilide is first produced by any suitable method but I prefer to mix 65 parts by weight of carbon bisulphide with 1 part of sulphur, and 120 parts of aniline is then added. The mixture is then brought to a temperature of about 35°–40° C. and kept at

Defendant's Exhibit QQ (Sheet

that temperature for several hours after which it is allowed to cool. The semi-solid mass resulting is then spread out to allow an evaporation of the excess of carbon bisulphide and to dry the thiocarbanilide.

The solvent is then prepared by heating about 60 gallons of alcohol having a specific gravity of from .850 to .900 in a suitable kettle or tank and then adding 50 lbs. of ammonium nitrate and the thiocarbanilide above mentioned. The tank is closed by a cover and the temperature of the mixture is gradually raised to about 50° C. and stirred continuously by a mechanically operated stirring device. When said temperature is reached 200 lbs. of litharge are then added and the stirring continued for about one hour, during which time the temperature is gradually raised to about 75° C. At this point a test quantity is withdrawn and tested for thiocarbanilide and if not positive a few pounds more of litharge are added and the stirring continued for a short time or until the desulphurization is complete. The contents of the tank is then allowed to settle, the alcohol drawn off and removed from the lead sulphide by a suitable filter press or other means. The alcoholic solution is then distilled to a specific gravity of .950 and then mixed while hot with about 125 gallons of water and the solution boiled for about one hour. This causes all of the diphenylguanidine nitrate to dissolve, leaving the heavy treacle-like mass of polymerized carbodiphenylimide undissolved excepting a small portion of the latter which goes into solution and which may be removed by adding one or two pounds of "filter-cel," which is distomaceous earth in the form of a powder used for the purpose of filtering. The solution is then syphoned off and allowed to cool, after which a 25% solution of caustic soda is added, while stirring vigorously until the precipitation is complete. When completely settled the supernatant liquid is drawn off, the diphenylguanidine is filtered out, washed with water and dried.

I have discovered that the diphenylguanidine thus obtained may be further purified for use in particular processes by dissolving and recrystallizing in toluol. The difference in the degree of solubility of diphenylguanidine in hot toluol over that when cold is very marked. It has been found that toluol at its boiling point will dissolve to form a 50% solution of this substance while cold toluol will dissolve only to about 2 per cent.

I therefore dissolve the diphenylguanidine in the portion of about 2½ lbs. of the latter to a gallon of toluol which is thus raised to a temperature of about 105° C. in a closed container. The hot solution is then filtered and allowed to cool, settle and to stand until crystallization is complete.

The crystals are then filtered out and washed several times with fresh or pure toluol to remove the remaining traces of the impurities. About 70 lbs. of pure diphenylguanidine is thus obtained.

Having described this example of the invention, I do not wish to be understood as being limited to the exact proportions, ingredients, temperatures, and steps set forth, for various changes may be made without departing from the essential features of my invention. For example, other solvents than alcohol may be used, such as wood alcohol, pyridine, etc., and other ammonium salts may be employed instead of ammonium nitrate above mentioned.

What I claim and desire to protect by Letters Patent is:

1. The process of making diphenylguanidine which comprises, desulphurizing thiocarbanilide by the use of a metallic oxide in an alcoholic solution of an ammonium salt.

2. The process of making diphenylguanidine which comprises desulphurizing thiocarbanilide by the use of a lead oxide in an alcoholic solution of an ammonium salt.

3. The process of making diphenylguanidine which comprises desulphurizing thiocarbanilide by the use of a lead oxide in an alcoholic solution of ammonium nitrate.

4. The process of making diphenylguanidine which comprises desulphurizing thiocarbanilide by the use of litharge in an alcoholic solution of ammonium nitrate.

5. The process of making diphenylguanidine which comprises dissolving an ammonium salt and thiocarbanilide in an alcoholic solution, then adding a lead oxide and heating to 75° C. to desulphurise the thiocarbanilide, then dissolving the diphenylguanidine nitrate thus formed, then separating the remaining carbodiphenylimide from said solution by causing precipitation with an alkaline solution, and then washing and drying the precipitate.

6. The process of making diphenylguanidine which comprises dissolving ammonium nitrate in an alcoholic solution, then adding litharge and heating to 75° C. to desulphurize the thiocarbanilide, then dissolving the diphenylguanidine nitrate thus formed, by distillation to a specific gravity of .950 and by addition of hot water, and then separating the carbodiphenylimide from said solution by causing precipitation by the addition of caustic soda, and then washing and drying the precipitate.

7. In a process of making diphenylguanidine the steps which comprise adding an alkali to a solution thereof containing carbodiphenylimide to cause precipitation, and then washing and drying the precipitate.

8. In a process of making diphenylguanidine the steps which comprise adding caus-

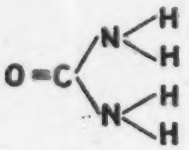
tic soda to a solution thereof containing carbodiphenylimide to cause precipitation, and then washing and drying the precipitate.

9. In a process of making diphenylguanidine containing as a reaction impurity carbodiphenylimide, the steps which comprise dissolving the same in hot toluol, cooling and then washing the crystals thus formed.

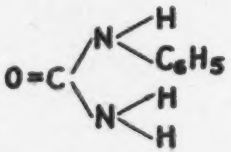
10. In a process of making diphenylguanidine containing as a reaction impurity carbodiphenylimide, the steps which comprise dissolving the same in hot toluol, cooling, and then washing the crystals thus formed with pure toluol, and then drying.

Signed June 28th, 1921.

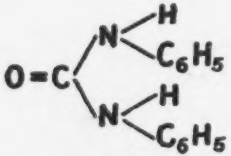
MORRIS L. WEISS



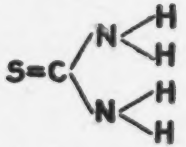
Urea



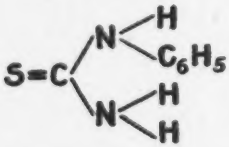
Monophenylurea



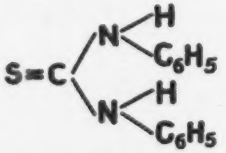
Diphenylurea



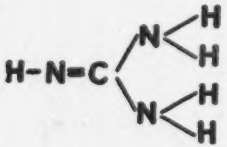
Thiourea



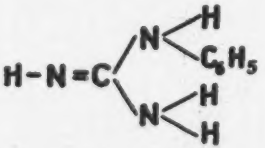
Monophenylthiourea



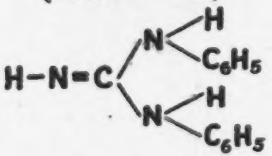
Diphenylthiourea
(Thiocarbanilide)



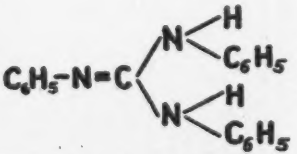
Guanidine



Monophenylguanidine



Diphenylguanidine



Triphenylguanidine

C Represents Carbon
H Represents Hydrogen
S Represents Sulphur
N Represents Nitrogen
O Represents Oxygen
C_6H_5 Represents Phenyl group

— (Lines) Represents "Valences" or bonds between atoms

Defendant's Exhibit QQ-1

When Morris L. Weiss came into the employ of the Republic Rubber Company I was doing research work on the guanidines and had developed triphenylguanidine.

When preparing to leave the employ of the Republic Rubber company I directed and advised the said Morris L. Weiss to proceed with research work on the phenylated guanidine derivatives, including monophenylguanidine and diphenylguanidine as well as the guanidine bases.

To the best of my knowledge and belief said Morris L. Weiss had had no knowledge or experience in accelerators for rubber prior to being employed by the Republic Rubber Company.

Clinton A. Carlton.

Subscribed and sworn to before me, this 3rd day of June, 1922. Pearl Piper, Notary Public. (Seal.)

Witness: H. H. Replogle.

The following depositions were stipulated from the case of Dovan vs. National Aniline and Chemical Co., Inc. (Stipulation, Rec., 577.)

SETH R. CLARK, called as a witness on behalf of the defendant, being first duly sworn, testifies as follows:

Direct examination.

By Mr. Edmonds:

Q. 1. Mr. Clark, in whose employ are you now?
A. I am with the Fisk Rubber Company.
Q. 2. In what capacity?
A. In the development department.
Q. 3. Have you an official title, and if so, what is it?
A. I have not.
Q. 4. Were you ever in the employ of the Republic Rubber Company?
A. I was for fifteen years.
Q. 5. When did that employment end?
A. In November 20th, 1920.
Q. 6. During 1919 who was in charge of the chemical laboratory of the Republic Company?
A. Mr. M. H. Daniels.

Q. 7. Was he under you?

A. He was.

Q. 8. And what was your official title?

A. My official title was assistant mill superintendent in charge of development work.

Q. 9. Did you know whether or not Morris L. Weiss was employed in the laboratory?

A. He was employed in the laboratory.

Q. 10. And was he under Mr. Daniels?

A. He was.

Q. 11. Can you state what work was being done throughout the first nine months of the year 1919 on rubber accelerators in the laboratory of the Republic Rubber Company?

A. Not definitely. We were carrying on continually work on accelerators.

Q. 12. Can you state what accelerators were being worked upon to a greater extent than others?

A. Yes, we had already constructed a house some few years before—a chemical department in which we made practically all of our thiocarbanilide, and had also constructed another chemical department in which we made triphenylguanidine, and at the end of that period, as I remember it, we had probably produced up to three hundred pounds of triphenylguanidine.

Q. 13. That is up to September, 1919?

A. Around in that date. I might explain that this way: I know that when Mr. Daniels left the employ of the Republic Rubber Company there were about two hundred pounds of triphenylguanidine on hand, as I remember it, that we had made in the laboratory.

Q. 14. And had made when?

A. During the latter part of 1918.

Q. 15. Did the work on triphenylguanidine continue through the first nine months of 1919?

A. It did.

Q. 16. Did that work practically come to an end at any time in 1919?

A. It came to an end in 1919 along towards the end of the year.

Q. 17. Will you state what the circumstances were in that connection as fully as you can?

A. I can. The company was more or less conservative in regard to the members of the company attending meetings and one thing and another like that, and I distinctly remember that to the meeting in Philadelphia Mr. Daniels went. On his return from that meeting, he partially, I suppose, for the purpose of justifying the trip, came to Mr. Brown and myself in our office and told us that the company was perfectly justified in sending him on the Philadelphia trip; that he had found out a lot about accelerators down there, and we asked him whether he had the dope and he said he did, and that he was immediately going to start work and——

By Mr. Cooper: I think this is all hearsay, if your Honor please.

By Mr. Edmonds: I think the witness should be allowed to finish first and the objection made afterwards.

By the Court: I think the objection is good.

By the Court:

Q. 18. Tell us what you did after you came back?

By Mr. Edmonds:

Q. 19. Will you continue only with respect to things that were said in your presence within your hearing?

By Mr. Cooper: That is all hearsay.

By the Court: What he did.

Q. 20. Then will you continue with your narrative only with respect to what you did, what Daniels did, what was done by the Republic Company?

A. We stopped work on triphenylguanidine and started experimental work on diphenylguanidine.

Q. 21. When was that?

A. In the latter part of 1919, immediately after Daniel's return from the Philadelphia meeting.

Cross-examination.

By Mr. Cooper:

X Q. 22. Who did the work?

A. The work was done under Mr. Daniel's supervision.

X Q. 23. By whom?

A. I have no idea.

X Q. 24. I did not understand what your connection with the Fisk Rubber Company is?

A. I am in the development department.

By the Court:

Q. 25. Is Mr. Weiss in that department under Daniels?

A. At the Republic Rubber Company?

Q. 26. Yes.

A. Oh, yes, in the chemical laboratory upstairs.

By Mr. Cooper:

X Q. 27. Daniels was downstairs and Weiss was upstairs?

A. Correct. We had the physical test laboratory downstairs and the chemical research laboratory upstairs.

X Q. 28. Do you not know that Mr. Weiss did work on D. P. G.?

A. I knew Weiss did some work in the laboratories, yes. I might explain my opinion of that work if you——

X Q. 29. No, I am not asking you for your opinion of the work.

A. The reason I say that is——

X Q. 30. When did Daniels leave the Republic Rubber Company?

A. I would say it was in March, 1920. It was when Mr. Jones came with the company as president; soon after that.

X Q. 31. Did you have anything to do while you were with the rubber company, with the keeping of laboratory records?

A. The laboratory records? Very little, as a laboratory compound was given to try out in the plant a whole lot.

X Q. 32. Are you a chemist yourself?

A. I am a graduate chemist.

X Q. 33. Whereabouts was your office at the Republic Rubber —?

A. My office was up on the second floor—at the period in question and for the last three or four years that I was with them my office was in the second floor of the five story building.

X Q. 34. The same building that has the chemical laboratories in them?

A. No, no, entirely apart from that.

X Q. 35. I suppose the plant was an extensive one?

A. Medium sized.

X Q. 36. Employing about how many hands during this period?

A. I should judge about 1,500 or 2,000.

X Q. 37. And how many buildings?

A. In the neighborhood of a dozen counting everything.

X Q. 38. And how far away was your five story building from the place where the laboratory was?

A. A couple of hundred feet.

X Q. 39. How often would you be in that laboratory building? Every day?

A. No, sir, not every day.

X Q. 40. Every week?

A. Yes, I would be there at least once a week.

X Q. 41. And was it your business to follow up the detail of what was done there, or just to talk to Mr. Daniels?

A. It was not.

X Q. 42. Mr. Daniels was the one who reported to you?

A. Yes, sir.

X Q. 43. You knew there were laboratory records kept there, did you not?

A. Absolutely. I put them into the factory.

X Q. 44. And do you know about this ex-laboratory book?

A. I know of ex-books that were used, yes, sir.

X Q. 45. Do you know something about some of the leaves being abstracted from one of those books?

A. Absolutely not.

X Q. 46. They were supposed to be all intact and kept as permanent records of the company?

A. Yes, sir.

X Q. 47. Was it after the receivership that you left?

A. No, sir.

X Q. 48. You left before the receivership?

A. Yes, sir, about five months.

SUR-REBUTTAL PROOFS

SETH R. CLARK, recalled as a witness on behalf of the defendant in sur-rebuttal, being previously sworn, testifies as follows:

Direct examination.

By Mr. Barrows:

Q. 49. Was there any general rule at the Republic Company regarding the entering of compounds in these laboratory X-books?

A. There always was a general rule.

By Mr. Cooper: Wait; I do not see that that is any rebuttal of anything.

By the Court: I will take it. What is the next question?

Q. 50. What were the instructions regarding the making of entries in these laboratory X-books?

By Mr. Cooper: I do not see how that enters into the matter.

By the Court: What is the purpose of this?

By Mr. Barrows: Mr. Weiss has said he made certain experiments and he did not put them in his laboratory notebook. I want to bring out that the instructions there were that all compounds should be put in the notebook.

By the Court: Say that, if it is so.

A. We had an absolute rule that the minute a man wrote out his compound on a rough piece of paper he should copy it in the book with the date, and in the first column of the experimental stock under which he was working, after he had labelled the page to indicate why the experiments were carried on.

Q. 51. And was there any general custom or rule regarding the placing of the dates on the notebook?

A. The rule was that the date was supposed to be put on when the man first made out his recipe. He sent his rough draft of the compound downstairs to the man who did the mixing. Then he had the copy in his book, so that if the man downstairs who did the mixing lost the recipes or anything, he would have his original records copied over into his book.

Q. 52. So that these laboratory X-books should contain all of the compounding tests which the man in charge carried out?

A. They absolutely should.

Cross-examination.

By Mr. Cooper:

X Q. 53. Well, do they? To your knowledge do they contain all the compounds that every expert connected with your company ever got up?

A. The testimony of your witness shows that they——

By Mr. Cooper: I move to strike that out.

By the Court: Strike it out.

X Q. 54. Do they contain it?

A. They should contain it.

X Q. 55. Do they?

A. I do not know.

JAMES W. KINSMAN, called as a witness on behalf of the defendant, being first duly sworn, testifies as follows:

Direct examination.

By Mr. Edmonds:

Q. 1. Mr. Kinsman, by what company are you employed at present?

A. I am employed by the E. I. Dupont de Nemours Company of Delaware.

Q. 2. Will you state your official capacity with that company?

A. I am now salesmanager in charge of the sales of dye stuffs, intermediates, organic chemicals, rubber vulcanizing accelerators, activating agents, and others of that group.

Q. 3. Did you ever hear of a paper read by Dr. Kratz and two of his associates at a meeting of the Chemical Society in September of 1919?

A. Yes, sir.

Q. 4. Will you state when and under what circumstances you became familiar with that paper?

A. I recall that early in June of 1920 Mr. Kratz who was associated and still is, I believe, with the Falls Rubber Company of Cuyahoga Falls, sent the Dupont Company an inquiry for various organic chemicals with which I assumed he wanted to experiment with to determine their properties as rubber vulcanizing accelerators.

I replied to Mr. Kratz and sent him as many of the articles as we had available and at the same time said that I recalled his giving an address before the New Jersey Chemical Society and asked if it was possible for him to give me a reprint of that article. Mr. Kratz replied promptly and sent two papers one of which was his address before the New Jersey Chemical Society and the other was his address before the American Chemical Society in Philadelphia in September, 1919.

Q. 5. Did you read that paper on receiving it, and if so, will you please state what it meant to you with respect to rubber vulcanizing?

By Mr. Cooper: It seems to me that is incompetent, what it meant to the salesmanager of organic chemical sales for Dupont.

Q. 6. What did you learn from your reading of that paper?

By Mr. Cooper: I do not think that is a competent question.

By the Court: I do not, either.

Q. 7. Will you state what you found in the paper with respect to the accelerating power of rubber accelerators?

By Mr. Cooper: Is that not calling for secondary evidence?

By the Court: Yes, it is secondary evidence. He can tell what he did afterwards.

By Mr. Edmonds: I am trying to avoid what we agreed should be kept out, this commercial exploitation by any of these companies.

By the Court: Where is the paper?

By Mr. Edmonds: It is the same Kratz paper we have been discussing. I have no objection to his telling the whole story of the Dupont entrance into this business but

I was trying to avoid that because of our agreement at the opening of this trial.

By the Court: I do not think you can ask him for the contents of the paper.

Q. 8. Did your company, the Dupont Company, enter upon the manufacture and sale of diphenylguanidine? Please answer yes or no.

A. Yes, sir.

Q. 9. Did it do that at a time subsequent to your receipt of this paper and prior to March 28th, 1922?

A. Yes, sir.

Q. 10. Has the company continued to manufacture and sell diphenylguan-dine since March 28th, 1922?

A. It has.

Cross-examination.

By Mr. Cooper:

X Q. 11. Just what was the date when the Dupont organization with which you are connected first put diphenylguanidine in the market?

A. I believe that the first sale we made was during the latter part of October, 1921, about the 26th or 27th.

X Q. 12. That was after the Dovan Chemical Company was on the market with the same product that you went into competition with them; is that not correct?

A. The only product I found that the Dovan Chemical Company had was a reduced form of what we determined in our laboratory to be diphenylguanidine. We put out a pure diphenylguanidine, which is what the trade asked us for.

X Q. 13. You got the Dovan Company's XLO product and analyzed it to find out what the substance was and then put that substance on the market; is that not correct?

A. No, sir.

X Q. 14. Go ahead and state what the fact was. You got a sample of this product of the Dovan Chemical Company and analyzed it.

A. We were interested in manufacturing diphenylguanidine because of inquiries from the trade.

By Mr. Cooper: I move to strike that out.
By the Court: Strike it out.

X Q. 15. I am asking you this. Did you get a sample of the XLO product of the Dovan Chemical Company?
A. Yes, sir.
X Q. 16. Did you have that analyzed?
A. Yes, sir.
X Q. 17. And by that analysis you determined the active properties of the XLO due to the diphenylguanidine in it, is that correct?
A. We found diphenylguanidine, but at that time we were not in position as rubber chemists to determine what was the activating agent.
X Q. 18. But you found diphenylguanidine?
A. Yes.
X Q. 19. And you found a demand for diphenylguanidine and then you proceeded to make it and sell it?
A. We found a demand for diphenylguanidine before we received the accelerator XLO.
X Q. 20. Then you found out what was in it and then went on the market yourselves. That is correct is it not? Yes or no.
A. We knew of the demand for diphenylguanidine before we got the samples of XLO.
X Q. 21. After you got the sample of XLO and analyzed it, then you went into the market yourselves.
A. Not as a result of receiving the sample.

By the Court:

Q. 22. Did you, yes or no?
A. We did.

Dedirect examination.

By Mr. Edmonds:

R. D. Q. 23. Was this all after you had received the copy of the Kratz paper?
A. Yes, sir.

ALFRED L. LOEBENBERG, called as a witness on behalf of the defendant, being first duly sworn, testifies as follows:

Direct examination.

By Mr. Edmonds:

Q. 1. Will you give your present employer and your official title?

A. I am production manager of the National Aniline & Chemical Company.

Q. 2. Have you ever met Morris L. Weiss, the patentee of the patent in suit here?

A. I have.

Q. 3. Will you say when?

A. I met him when he applied to us for a position.

Q. 4. For a position with the National Aniline, the defendant here?

A. That is right.

Q. 5. On that occasion was anything put in writing in connection with his application?

A. There was.

Q. 6. State generally what it was?

A. The formal application blank of the National Aniline.

Q. 7. Look at that document, please, and say what it is?

A. That is the application form.

Q. 8. Do you know whose handwriting is there?

A. Mr. Weiss's handwriting.

Q. 9. Did you see him write that?

A. Yes.

Q. 10. Whose handwriting appears on the back of that sheet?

A. My own.

Q. 11. Can you state anything about your conversation with Weiss at the time this application was made outside of the usual data filed in in the blanks on the front of this application?

A. Mr. Weiss in applying to us for a position qualified himself as a man experienced in rubber chemistry; stated that he had done some research, that is, development work in the manufacture and application of certain rubber accelerators. At the time I noticed the accelerators to

which he specifically referred. The accelerators included aniline, thiocarbanilide, triphenylguanidine, diphenylguanidine, nitroso dimethyl aniline.

Q. 12. That I take it is the part referred to at the top of this sheet?

A. That is correct.

Q. 13. What is referred to lower down on the sheet?

A. In the course of our conversation Mr. Weiss, discussing rubber accelerators in general, stated that he had developed a process for the manufacture of diphenylguanidine and he wanted to interest us in that process, that is, with a view toward manufacturing it commercially. The process, he said, had been developed by him.

In the course of that conversation he referred to diphenylguanidine as an accelerator which apparently was known in that he referred to some ratios of value of diphenylguanidine and other accelerators, and I made a notation at that time of a reference to Dr. Kratz, who as I remember had made reference to the relative values of various accelerators including according to this notation, aniline, thiocarbanilide, diphenylguanidine, triphenylguanidine and hexamethylin tetramine. The conversation with Mr. Weiss revolved to a certain extent on the question of interesting us in this process.

By Mr. Cooper: I will object to that. Let the witness say what he said.

By the Court: Yes, strike it out.

(A. to Q. 13 continued.) Mr. Weiss, in qualifying himself for this position which he was seeking with us, attempted to introduce——

By the Court:

Q. 14. What did he say? Tell us what he said.

A. He stated that diphenylguanidine was a very valuable accelerator in that it offered certain advantages over other accelerators which had been used, and he inquired whether we would be interest- in developing that particular process as a commercial proposition.

By Mr. Edmonds:

Q. 15. Reference was made to Dr. Kratz?

A. A reference was made to Dr. Kratz.

Q. 16. Does Dr. Kratz's name appear written on the back of that sheet?

A. It does.

Q. 17. And who wrote it there?

A. I wrote it.

Q. 18. At that time?

A. At that time.

Q. 19. Was there any discussion as to who had originated the use of diphenylguanidine as an accelerator?

A. There was not.

By Mr. Edmonds: I offer in evidence the application identified by the witness's testimony.

(Marked Defendant's Exhibit M, attached to affidavit of Loebenberg file.)

Cross-examination.

By Mr. Cooper:

X Q. 20. How many candidates for a technical position have you seen in the last two or three years?

A. Oh, possibly fifty to one hundred, I should say.

X Q. 21. This pencil writing on the blank side of this form that you say Dr. Weiss filled out, is in your handwriting?

A. My handwriting.

X Q. 22. All of it?

A. Every bit.

X Q. 23. Including the arrow and the "Dr. Kratz"?

A. That is right.

Robert L. Moore, called as a witness on behalf of the defendant, being first duly sworn, testified as follows:

Direct examination.

By Mr. Edmonds:

Q. 1. What is your full name?

A. Robert L. Moore.

Q. 2. Your age?

A. Twenty-seven.

Q. 3. Where do you live?
A. Pittsburgh, Pennsylvania.
Q. 4. What is your occupation?
A. Chemist.
Q. 5. Were you ever employed by the Falls Rubber Company?
A. Yes, sir.
Q. 6. When?
A. In 1917.
Q. 7. What time in 1917 did you go there?
A. In May.
Q. 8. And how long did you stay?
A: I left there the latter part of September, the same year.
Q. 9. What were your duties?
A. I was was an assistant to Mr. Kratz.
Q. 10. Do you recall a batch of one thousand gray tubes that were made while you were employed there?
A. I do.

By Mr. Cooper: I think that is rather a blunt way of putting a proposition that may be of the utmost importance to the outcome of the case.
By the Court: Do you object?
My Mr. Cooper: I do.
By the Court: Objection overruled.

Q. 11. I show you a paper marked Defendant's Exhibit K for identification and ask you if you can tell what this sheet is?

By the Court:

Q. 12. Is that in your handwriting?
A. Yes, sir.
A. (to Q. 11) This is a test sheet which I made in August, 1917, at the Falls Rubber Company laboratory.

By Mr. Barrows:

Q. 13. Do you know what the compound was that was used in this test other than that it was marked "T-63"?
A. Why, it was a gray inner tube stock T-63 that we were experimenting with at that time.

By Mr. Barrows: I would like to offer this sheet in evidence.

(Defendant's Exhibit K, for identification, marked in evidence.)

Cross-examination.

By Mr. Cooper:

X Q. 14. The fourth column on the left headed "Dimensions of Test Piece—Thickness—Width"—are those figures expressed in inches?

A. Yes, 64th of an inch.

X Q. 15. The thickness is 9/64ths?

A. Yes, sir.

X Q. 16. That was a gray inner tube, was it?

A. No, it was not. It was a sample of a stock which was going into inner tubes. It was a slab procured for test purposes.

X Q. 17. These you had were 9/64ths of an inch thick, 13/64ths wide?

A. Yes, the test piece was dyed out 13/64ths wide.

X Q. 18. You do not know the length?

A. The length of the test piece?

X Q. 19. Yes, the larger tubular dimensions?

A. Standard length test piece.

X Q. 20. Square?

A. No, it is what we call a dumbell shape. The ends are large and then it is constricted down to about a quarter of an inch width in the middle, where the break actually occurs. That is standard practice on this machine.

X Q. 21. Its original length was 12.5 inches, or whatever the figure is?

A. That is in percentages. That is not in inches. That is the permanent set for the amount that the test piece gained by the stretching during the machine testing.

X Q. 22. What are these tests supposed to be good for?

A. They evaluate the quality of the stock, give us a definite idea in comparing this stock with another stock in experimental work in the laboratory.

X Q. 23. Is this what you would denominate a low grade or a high grade mixture?

A. It was a low-priced stock at that time.

X Q. 24. By low-priced, you mean low grade?

A. No, not necessarily. The stock was of average quality.

X Q. 25. That is, average quality in comparison with other products?

A. For that type of stock, yes.

X Q. 26. Was it average quality for the Falls Rubber Company's production at that time?

A. No, I would not say that. I do not believe it was.

HENRY V. MORSE, called as a witness on behalf of the defendant, being first duly sworn, testifies as follows:

Direct examination.

By Mr. Edmonds:

Q. 1. You are employed by what company?

A. Atlantic Dye Stuff Company.

Q. 2. What is your position with that company?

A. I have charge of the accelerator department.

Q. 3. Will you state whether or not you attended the Philadelphia meeting in September, 1919, when the Kratz paper on rubber accelerators was read?

A. I did.

Q. 4. Prior to that time had you been engaged in work on rubber accelerators?

A. I had.

Q. 5. Prior to March 28th, 1922, did your company put diphenylguanidine on the market?

A. I cannot recall.

Q. 6. Can you state whether or not your company had made preparations for doing so prior to that date?

A. We had been making preparations.

Q. 7. Has your company put that product on the market?

A. It has.

Q. 8. And from the time it started to the present time, has it kept on the market continuously?

A. It has.

Cross-examination.

By Mr. Cooper:

X Q. 9. At the time that you were preparing or that your company was preparing to put diphenylguanidine on the market, you knew of the Dovan Chemical Company and its product?

A. I did not.

X Q. 10. Never had heard of it?

A. No, sir.

X Q. 11. Did you know that the Dupont concern had diphenylguanidine on the market?

A. I did not.

X Q. 12. You did not know that any other concern had?

A. Not at the time we were preparing about it.

X Q. 13. Did you know the States Metals Company?

A. Yes, sir.

X Q. 14. Did you know what if was putting out?

A. I know it was putting out a compound called XLO.

X Q. 15. Did you get a sample of that?

A. I did.

X Q. 16. You do not know anything about what was in that sample?

A. I knew what was in it.

X Q 17. What?

A. Diphenylguanidine and magnesia.

By Mr. Cooper: Before I forget it, you will not dispute my statement appearing in the injunction motion papers that the States Metals Company was the selling agent of the Dovan Chemical Company?

By Mr. Edmonds: No.

William F. Russell, called as a witness on behalf of the Defendant, being called first duly sworn, testifies as follows:

Direct examination.

By Mr. Barrows:

Q. 1. What is your full name?

A. William F. Russell.

Q. 2. Your age?
A. Thirty-five.
Q. 3. Where do you reside?
A. Norwalk, Connecticut.
Q. 4. What is your occupation?
A. Chemist.
Q. 5. Where are you employed?
A. Norwalk Tire & Rubber Company.
Q. 6. And what is your position there?
A. Chief Chemist.
Q. 7. How long have you been Chief Chemist?
A. Since 1914.
Q. 8. At the Norwalk Tire & Rubber Company?
A. Yes, sir.
Q. 9. Do you know George D. Kratz?
A. Yes, sir.
Q. 10. And was he ever employed by the Norwalk Tire & Rubber Company?
A. Yes.
Q. 11. Were you acquainted with the work which Mr. Kratz was doing in the latter part of the year 1916?
A. Yes, sir.
Q. 12. What was your relation to him at that time?
A. Mr. Kratz was my chief assistant.
Q. 13. And were you familiar with the work he was doing?
A. Absolutely.
Q. 14. I hand you Defendant's Exhibit E and ask you if you can tell what these are and where they were obtained from?
A. These are records of certain work which Mr. Kratz did at that time and which were left in the report book of his work in general, placed in the files of the laboratory.
Q. 15. And these were produced from the files of the Norwalk Tire & Rubber Company?
A. Yes, they were taken from those files.
Q. 16. By you?
A. Yes, sir.
Q. 17. Do you recognize the handwriting on these sheets?

By Mr. Cooper: I object to that. The other man identified it as his handwriting. I do not question that.

Q. 18. Do you know that the work described on these sheets was done by Mr. Kratz in the year 1916?

A. Yes, sir.

Q. 19. Were you familiar with the work he was doing at that time?

A. Absolutely.

Q. 20. How closely in touch were you with this work?

A. We had conversations on it practically every day.

Q. 21. What was your relation to him at that time officially?

A. Officially I suppose I was his superior officer.

Q. 22. And you knew of the results which he obtained and which are described on these sheets?

A. Yes, I knew of them.

Q. 23. Do those records show that diphenylguanidine is an accelerator for the vulcanization of rubber?

By Mr. Cooper: I object to that.

By the Court: Objection sustained.

Q. 24. Do you know why Mr. Kratz used the particular mixtures he did to carry on these experiments?

By Mr. Cooper: I object to that.

By the Court: Objection sustained.

Q. 25. Do you know how many tests Mr. Kratz made on diphenylguanidine prior to the reports of the work described in these reports?

A. I cannot remember exactly. Do you mean on diphenylguanidine alone?

Q. 26. Yes.

A. I should say probably he did anywhere from eight to ten or perhaps twelve experiments.

Q. 27. Do you know what tests Mr. Kratz made on the vulcanized samples that he produced using diphenylguanidine as an accelerator?

A. I did not get that.

Q. 28. Do you know what tests he made of the vulcanized products, the vulcanized rubber made with diphenlyguanidine?

A. Physical tests?

Q. 29. Yes.

A. Yes.

Q. 30. What were these tests?

A. We used the ordinary thumb and tooth test as it is called, which rubber chemists are in the habit of using for estimating the quality of their stocks.

Q. 31. And you still use those tests?

A. We still use those tests.

Q. 32. You were subpœnaed by the plaintiff, the Dovan Chemical Corporation, to be in attendance, were you not?

By Mr. Cooper: I object to that.

By the Court: What difference does it make. He is here to tell the truth.

A. I was.

Cross-examination.

By Mr. Cooper:

X Q. 33. Is the thumb and tooth test the only one used in your company, Doctor, to test a new sample or degree of rubber?

A. No, sir.

X Q. 34. What else?

A. We have another method of testing when we want to express our result in figures, the machine method of testing.

X Q. 35. Do you regard that as satisfactory when you are trying to arrive at a determination whether to use a new mix or not?

A. No, sir.

X Q. 36. With a thumb and tooth test and a machine test, do you determine by the result of those alone whether you will put a new experimental mix into production?

A. I would determine by the thumb and tooth test alone whether I would put a new compound into use in the factory.

X Q. 37. After those tests to which you have referred of Mr. Kratz's sample, did you put the diphenylguanidine mixed into commercial production in the factory?

A. We did not.

X Q. 38. When if ever did your company first begin to use diphenylguanidine in commercial production?

A. We never used diphenylguanidine in commercial quantities.

X Q. 39. You have always used some other accelerator if you used an accelerator at all?

A. We have.

Redirect examination.

By Mr. Barrows:

R. D. Q. 40. Why is it that you have not used diphenylguanidine commercially at Norwalk?

By Mr. Cooper: I object to that. I think it is incompetent.

By the Court: I will take it. Objection overruled.

A. We never used it commercially on account of the fact that we saw no advantage in displacing the accelerators we were then using by diphenylguanidine.

NORMAN A. SHEPARD, called as a witness on behalf of the defendant, being duly sworn, testifies as follows:

Direct examination.

By Mr. Edmonds:

Q. 1. Give the name of your present employer?

A. Firestone Tire & Rubber Company.

Q. 2. How long have you been in the employ of that company?

A. Since April, 1919.

Q. 3. And what is your capacity there now?

A. I am in the research laboratory, Director of Organic Research.

Q. 4. Did you attend the meeting of the Rubber Section of the Chemical Society in Philadelphia in September, 1919?

A. I did.

Q. 5. You heard the Kratz paper which we have discussed here read?

A. I did.

Q. 6. Will you state whether or not any of the tables included in the paper were displayed at the time the paper was read?

By Mr. Cooper: I will object to that. I do not see what difference it makes whether the tables were displayed or not. The paper was read, Kratz said it was, and we have not any disposition on our part to contradict Kratz.

By the Court: I will take it.

A. Certain tables were put on the blackboard.

Q. 7. Did you take copies of them?

A. I made some notes of these tables.

Q. 8. Do you know whether that was done by others around you?

By Mr. Cooper: I will object to this, if your Honor please.

By the Court: If he knows of his own knowledge, he may state.

Q. 9. Do you know of your own knowledge whether others in the audience took copies of that table?

A. I believe they did.

Q. 10. Did you receive a copy of the paper in print later on?

A. Reprint, you mean?

Q. 11. Reprint, or in the magazine which was published?

A. I read it in my personal copy of the magazine.

Q. 12. Were you familiar generally with the literature of accelerators at that time?

A. I was.

Q. 13. Will you state whether or not any publication had come to your attention up to that time including such figures as were given in the table included in the Kratz paper?

By Mr. Cooper: I will object to that as incompetent.

By the Court: He say state what it meant to him.

Q. 14. Will you state in your own way just what the Kratz paper meant to you as a rubber chemist?

A. This paper was the first paper which gave us any definite idea of the relative activity of accelerators and as such was an extremely important paper, because having these relative activities we were enabled to apply the various accelerators sensibly.

Q. 15. Along in the following year 1920 did you meet Mr. Weiss?

A. I did.

Q. 16. About March 3rd, 1920?

A. I believe that was the date; early in March.

Q. 17. Had you met him before that time?

A. I had not.

Q. 18. Will you state what occurred on March 3rd, so far as concerns yourself and Mr. Weiss?

By Mr. Cooper: Where was this meeting?

Q. 19. Will you start off by saying where the meeting occurred?

A. In the lobby of the Firestone Tire & Rubber Company.

Q. 20. And what was the occasion for the meeting?

A. Mr. Weiss applied for a position in our Research Laboratories.

Q. 21. Were you in need of further assistants in the research laboratory at that time?

A. We were.

Q. 22. When this application was made were you instructed to see him?

A. I was.

Q. 23. By whom?

A. By the chief chemist.

Q. 24. And did you see him?

A. I did.

Q. 25. Where did you see him?

A. I saw him in the lobby of the Firestone Tire & Rubber Company.

Q. 26. And did your conversation from that time on take place in the lobby?

A. In the lobby of the Firestone Company.

Q. 27. Did you ask Mr. Weiss what qualifications or experience he had that would warrant you in giving him a position?

By Mr. Cooper: Let him state the conversation or what the substance of the conversation was.

By the Court:

Q. 28. What did you say?

A. He gave me first his training—Brooklyn Polytech, Columbia University; presented at least one reprint of previous work; then he stated that he had worked out a method for the preparation of an important accelerator, and showed me the typewritten copy of his work, which was a report of the Republic Rubber Company. This was his chief argument—or he considered it his chief asset in seeking a posi-

tion with the Firestone Company. He made no mention of having discovered this material as an accelerator. In fact, he ascribed the discovery to Mr. Kratz.

By Mr. Cooper: I will object to that last. I think the witness should say what he said.

By the Court: Yes, strike it out.

Q. 29. Just tell us exactly what he said.

By Mr. Edmonds:

Q. 30. Will you state as a matter of fact, whether or not in the course of your conversation with Mr. Weiss he made any claim to have originated the idea of using diphenylguanidine as an accelerator?

A. He did not.

Q. 31. In the course of that conversation was anything put in writing?

A. The usual application was filled out.

Q. 32. Is the paper I hand you the application referred to?

A. That is the application.

Q. 33. In whose handwriting is it?

A. Mr. Weiss's handwriting.

Q. 34. How do you know that that is Mr. Weiss's handwriting?

A. Why, it is my recollection that he filled that out in my presence.

Q. 35. Do you recall whether or not you saw him write the matter appearing on the first page?

A. I do not recall whether I left Mr. Weiss in the lobby at the table writing this application.

Q. 36. If you left him, did you see him further after leaving him?

A. I did.

Q. 37. At that same time while he was there at the Firestone Company on that visit?

A. I must have, because this application was handed to me.

Q. 38. Have you read the matter appearing on the first page?

A. I have.

Q. 39. Was that matter the subject of conversation between you and Mr. Weiss?

A. It was.

Q. 40. At that time when that application was made out?

A. Yes.

Q. 41. Can you recall anything further about your conversation with Mr. Weiss on the subject of the Kratz paper or anything done by Mr. Kratz additional to what is on that paper?

A. I do not recall any further conversation.

By Mr. Edmonds: The application referred to by the witness is offered in evidence in behalf of the defendant.

(Marked Defendant's Exhibit L.)

Cross-examination.

By Mr. Cooper:

X Q. 42. You mentioned on your direct examination that when Mr. Weiss came for a job, he showed you what you described as a typewritten report that he, Weiss, had made to the Republic Rubber Company. Is this the document?

A. That is the document, I should say.

X Q. 43. I do not want to have any doubt in your mind about it?

A. I believe the cover is missing.

X Q. 44. Well, you identify that as a document that he handed you on that occasion?

A. That, or a copy of it, I believe.

X Q. 45. Did he leave it with you?

A. He did.

X Q. 46. Did you examine it?

A. I did. I examined it in his presence and later.

X Q. 47. I understood you to say that after hearing Kratz's paper you got considerable interest in the subject of accelerators for rubber; is that correct?

A. Before that time I spent most of my time on accellerators for rubber.

X Q. 48. Did that stimulate your interest?

A. My interest could not be stimulated beyond what it was.

X Q. 49. I mean, along any particular lines?

A. Particular lines? Naturally, I was interested in those particular substances which he had mentioned in giving us specific information on.

X Q. 50. Which one?

A. Which one? The guanidine series interested me most of all.

X Q. 51. And from that time on did you take more interest in the guanidine series than you had before?

A. I would not say so. I was interested in the guanidine series.

X Q. 52. Had you yourself discovered the excellence of each member of the guanidine series with reference to its accelerator properties in the curing of rubber?

A. I had not.

X Q. 53. Was Gratz's paper the first knowledge you had in a detailed and scientific way of the facts in that regard?

A. It was the first detailed knowledge.

X Q. 54. Now, it was about six months after that that Mr. Weiss came to apply for a position, was it not?

A. In March.

X Q. 55. And up to that time had your company used diphenylguanidine as an accelerator for rubber?

A. It had not.

X Q. 56. Or any of the guanidine series?

A. We had been studying the guanidine series for some time.

X Q. 57. Since that time has the Firestone Tire & Rubber Company used diphenylguanidine as an accelerator for rubber?

A. It has not.

X Q. 58. Never has used it?

A. Only as we are using it experimentally today.

X Q. 59. Any of the other of the guanidine series or groups or whatever you may call it?

A. We have used other members of the guanidine series.

X Q. 60. Commercially?

A. Yes.

X Q. 61. What are you now using commercially?

By Mr. Edmonds: If your Honor please, I think I will have to object to asking this witness questions about what the Firestone Company is actually using. I cannot think of any ground on which that would have any relation to the issues in this suit, and everyone in this industry has been told of one other patent for which rather extravagant claims

are made, and evidence of the use commercially of such accelerators might have a bearing on issues which arise in some other suit, whereas they could have no bearing in this suit.

By the Court: I will sustain the objection.

X Q. 62. Did you ever test the truth of Mr. Weiss's statements as he made them in this paper?

A. The truth of Mr. Weiss's statements?

X Q. —. Yes; as he made them in this application blank?

A. I did not.

X Q. 64. Did you ever give his application any real consideration whatever or did you just pocket the whole thing?

A. I gave it real consideration.

X Q. 65. Did you write to him and say that his application was refused?

A. I did.

X Q. 66. How long afterwards?

A. I could not say. I should say it was within a week.

X Q. 67. Did you endeavor to ascertain in that period of a week before you turned him down whether at the Republic Rubber Company he had developed a process for the manufacture of thiocarbanilide which is worked successfully now in preference to the old process?

A. I took his word for it, naturally.

X Q. 68. Did you test the correctness by reference to the Republic Rubber Company of his statement that he had lately developed a process for the commercial production of symmetrical diphenylguanidine?

A. I did not.

X Q. 69. Did he say anything more to you specifically about Dr. Kratz than appears on the face of this application to the effect that the value of this product (referring to diphenylguanidine) as an accelerator has been discussed by Dr. Kratz at the Philadelphia Meeting of the American Chemical Society?

A. In bringing up the value of the work he had done on the method of preparation he stated, "Of course, you know that diphenylguanidine is a good accelerator from what you have heard at the Philadelphia meeting."

X Q. 70. And that is the substance of what you understood, is it not, from the statement in this application that

the value of this product as an accelerator has been discussed by Dr. Kratz at the Philadelphia meeting of the American Chemical Society?

A. Yes.

X Q. 71. Have you studied the statements in this application made by Dr. Weiss and in this typewritten report that he submitted to you and which you returned to him to determine whether the statements are correct so far as they refer to diphenylguanidine?

A. Studied? I doubt whether I have ever studied that. I read that report. I believe the statements in it are correct.

By Mr. Cooper: I offer this paper in evidence.

(Marked Plaintiff's Exhibit No. 8.)

Clerk's certificate to foregoing volume of exhibits omitted in printing.

[Caption omitted]

In United States Circuit Court of Appeals for the Third Circuit, October Term, 1926

No. 3470

Dovan Chemical Company, Plaintiff Below, Appellant,

vs.

Coroma Cord Tire Company, Defendant Below, Appellee

On Appeal from the District Court of the United States for the Western District of Pennsylvania

Before Buffington, Woolley, and Davis, Circuit Judges

Opinion—Filed December 7, 1926

Buffington, Circuit Judge:

This case concerns the acceleration of rubber vulcanization. As the patent here involved and the art to which it

appertains has been set forth at length in an opinion reported at 292 Fed. Rep. 555, a case in the Second Circuit involving the same patent and also in the exhaustive opinion of the Court below in this case, reported at 10 Fed. Rep. (2d) 598, we avoid repetition by referring thereto. The proofs show that Morris L. Weiss, the grantee of the patent here involved, was a chemist employed by a rubber company. During the course of his work and moved by a suggestion in Richter's Chemistry, Weiss, in March, 1918, conceived the idea that a well-known laboratory product, diphenylguanidine, known by the chemical symbol D. P. G., and listed by Richter but not as an accelerator, might be used in accelerating the vulcanization of rubber, and then so told Carlton, the chief chemist of the factory. The chemical properties of D. P. G. as a laboratory element, were of course known as an abstract truth, but no one prior to Weiss seems to have conceived and worked out any practical plan by which D. P. G's potential powers could be commercially used. The reason for this is plain for no one knew, or, for that matter, had tried to learn, how D. P. G. could be produced in such quantity as to make possible its commercial use. Having conceived the general idea and made at the factory where he was employed some recorded laboratory experimental work under various dates, Weiss took up the problem of trying out D. P. G. as a vulcanizer and of devising some way to make D. P. G. in such quantity that it could be practically used commercially. The problem was untried and difficult. He first set about making laboratory D. P. G. and in September, 1918, Weiss had produced five grams which by December he had tested with the ordinary rubber batches and found it powerfully accelerated but the rubber product was overcured. However, he was encouraged by them and shortly thereafter his experiments resulted in a perfect cure which was recorded in an experimental book under date of February 10, 1919, a date which as we shall hereafter see is challenged as being changed to that date from September 10, 1919. Under date of February 21, 1919, another successful test, this time with a shoddy compound, was entered in the same book and another with shoddy on March 4, 1919. Those experiments proved the workable worth of D. P. G. as an accelerator in vulcanizing rubber, but Weiss stopped work-

ing further in that line as his supply of D. P. G. had been exhausted. He then turned his attention to discovering some way to make D. P. G. commercially. His efforts in that line resulted in his discovery disclosed and practically utilized in the patent in suit. We here note that he was told he could not get a patent for an accelerator, but, later on, finding he could patent his original discovery, he applied on November 12, 1921 for a patent thereon and on March 28, 1922, was granted the patent in suit, No. 1,411,231. This patent, regularly granted, under the authorities, is prima facie evidence of its validity and unless successfully challenged warrants a decree in this case as infringement is clear.

Such attack is here made and is based on two grounds, viz: first, denial of patentable invention and second, that, if patentable, Weiss was not the original inventor thereof.

Addressing ourselves to the question of patentable invention, we find ourselves in accord with the patent office's action in the grant of the patent. In the first place the worth of D. P. G. as an accelerator is evidenced in its use by the defendant, by the mass of testimony, array of counsel and earnest effort here very properly made to ensure its continued use by this litigation. Its use has been extensive in the art, it has reduced the time of vulcanization, obviated overcuring and increased the character and worth of the product. These elements, while not conclusive, are evidential of its worth in the art. Assuming for present purposes the prima facies of Weiss' patent stands, and the statement in his specification: "I have discovered that disubstituted guanidines particularly diphenylguanidine is particularly effective for this purpose" is true, and if he showed the world in addition how to make this product in commercial quantity in the rubber vulcanizing art, it would seem to us and we so hold, that a claim, such for example as his eighth, viz: "The process of treating rubber or similar materials, which comprises combining with the rubber compound a vulcanizing agent and diphenylguanidine," was inventive in character and valid. In that regard we agree with Judge Manton's holding, when this patent was before him in the Second Circuit, that it involved invention, viz:

"I am satisfied that the use of diphenylguanidine as in the plaintiff's process, involved invention. Using it ad-

vanced the art of rubber making. Its utility and the consequences which followed, fully support the real practical test of the sufficiency of an invention. Where the utility is proved to exist in any degree, a sufficiency of invention to support the patent must be presumed. (Smith vs. Goodyear, 93 U. S. 486.) This substitution involved a new process of manufacture to develop a new use of the properties of diphenylguanidine and there was a new and useful result obtained. (See Smith vs. Goodyear, supra; Rumford Chemical Works vs. N. Y. Baking Powder Co., 134 Fed. 385; Genl. El. Co. vs. Hoskins Mfg. Co., 224 Fed. 464.)"

The process then being new, useful and inventive in character, it remains to inquire whether the prima facies of inventorship which the patent vested in Weiss is overcome by proof of the standard the law requires, that someone else was the inventor thereof. Turning then to the patent to see what Weiss disclosed and, consequently, what alleged prediscoverers must convincingly prove they had discovered and disclosed before him, we note the specification states generally: "The object of my invention is to improve rubber compounds so that the finished product shall be of superior quality and so that the time required for vulcanization shall be greatly reduced over that ordinarily required for such purpose. * * * I have discovered that di-substituted guanidines particularly diphenylguanidine is particularly effective for this purpose. * * * Down to the time of my researches in accelerators of this type, it was apparently not known that di-substituted guanidines were efficacious or useful as accelerators in vulcanizing, nor that this substance could be produced in sufficiently large quantities in a substantially pure form, or at a sufficiently low cost to be available for this purpose."

The specification then states that in another patent, viz: Serial 482,143, he has disclosed "a process for producing and purifying diphenylguanidine in commercial quantities" and after disclosing fully how, in what proportions and under what heat conditions, the D. P. G. was to be used, Weiss set forth desirable results thereby obtained, viz:

"It will therefore be appreciated that when using the accelerator according to my invention the vulcanization

is accomplished by using comparatively small quantities of the accelerator, thereby obviating undesirable loading or adulteration of the rubber compound. Furthermore, by the use of such accelerator, the texture and durability of the final product is greatly improved and the tendency commonly present in vulcanized rubber to bloom and become brittle with age is greatly reduced if not entirely obviated. My improved accelerator is particularly useful and valuable, where it is desired to produce a harder or less elastic portion in an article leaving other parts which are required to be more elastic and flexible, such as in automobile tires where the beadstock is usually made harder than the body or carcass of the tire proper. The relative amounts of vulcanizing agent and accelerator may be so proportioned that the various parts of a single article may be cured to different degrees of hardness without danger of over-curing the softer or more elastic parts."

It will thus be seen that summarized Weiss' claim of invention was, first, that no one before him had known that D. P. G. was efficacious or useful as an accelerator in commercial vulcanizing; second, no one had known that D. P. G. could be produced in quantity, in pure quality or at a cost to permit its use in vulcanizing; third, that Weiss was the first to solve this second problem by his patent No. 482,143; fourth, that the solution of this second problem enabled him, for the first time in the rubber vulcanizing art, to commercially use D. P. G.

Without entering into details and a discussion of the proofs we may say they satisfy us that Weiss was the first to instruct the rubber art in this mode of rubber vulcanization and that up to his work the rubber art had made no use of D. P. G. in vulcanization and no one had therefore disclosed to the art or instructed it how D. P. G. could be practically produced or, of course, practically used. As showing the foremost advance, knowledge and practice in the rubber art in that regard, we take the exhaustive paper prepared by Dr. G. D. Kratz and his associates and read by him on September 2, 1919, at a meeting of The American Chemical Society in Philadelphia and published in April, 1920, in the Journal of Industrial & Engineering Chemistry. We feel justified in regarding this paper as evidencing not only

the highest point of advance by the art in general but the highest point reached by the three men in their individual prior research and practical results attained. Here was a convention of the leading scientific minds of the rubber industry; here was an opportunity to disclose an invention of vast importance to that art, if it had been made, and to give the public instructions in a novel and untilled field, and in that field, barren of any attempt to use D. P. G. Therefore, to assert inventive priority and to foreclose all subsequent claimants of invention in that regard by there announcing and showing the thing had been done, was now disclosed and the art enabled to now use D. P. G., was an opportunity not to be neglected.

Assuming for present purposes that Dr. Kratz and his associates had conceived the idea of the practical and commercial use of D. P. G. in the rubber art, did this paper so state? Conceiving they had devised some way to make D. P. G. commercially, did the paper tell the art how it could be done? That the paper did not give such information is clear. A contemporaneous report of the meeting and the paper in question made to his company by Williams, a chemical representative of a rubber company, who attended the meeting, may be taken as illustrative of the effect it made on the most highly skilled minds in the art, for after giving an analysis of what the paper meant to him, in which we find no such disclosure as Weiss made in his patents, Williams adds: "The symposium on the action of accelerators which followed was unimportant as every one seemed to try to conceal all he knew on the subject, but obtained all the information possible from others." And indeed that withholding of information from the rubber art, and not disclosure of a workable advance was the very purpose of the paper of the authors and was testified to by one of their number who said:

"We absolutely had no intention of giving any information which any other company or competitor could transpose directly for practical purposes. Our idea, however, did give enough information so that any reputable chemist would be guided by the information in the paper.

Q. Guided to the extent of being put on inquiry, to find out for himself anything you did not say—is that right?

A. Guided to the extent of stimulating investigation along the same lines with which we were pioneering.

Q. And without telling him what to investigate?

A. No, sir. We gave him two tables of what to investigate.

Q. But, I mean, you did not tell him any specific substance to investigate?

A. Well, we gave him two tables of substances, which we pointed out were excellent accelerators.

Q. And he could take his choice from any one of the substances mentioned in the two tables?

A. Absolutely.

Q. And go on investigating for himself?

A. Yes, sir, because there is no one accelerator of universal application or universal quality."

And this estimate by Dr. Kratz of the purpose of the paper, namely, an invitation to experimental research, is evidenced by what influence the paper had in the case of Weiss personally Daniels, who was Weiss' Chief, attended the meeting in Philadelphia and took notes of the tables in the paper, and on his return, as he testified, he did "immediately tell Weiss that the statements made in the paper read by said Kratz confirmed our experience with D. P. G. as to accelerating, and that we should continue to work on that substance and develop a commercial process if possible."

It will thus appear that the paper of Kratz and his associates had no effect on the working art. No one made any practical use of it. No one in the art selected D. P. G. from the several accelerators named in its tables and used it in the vulcanization of rubber. No special emphasis was laid on D. P. G. in comparison with other substances so named and it is quite evident that if advance in the art had stopped with the Philadelphia paper the art would not have had the information and advance disclosed by Weiss in his patent specification and would not have made the successful advance which followed Weiss' disclosure. Such being the negative results produced by the paper, we cannot accede to the proposition that its theoretical statements, valuable as they were, forestalled or even fore-shadowed the clearcut, practical conception which Weiss then purposed and which he later practically worked out, namely the

successful pioneer making of D. P. G. commercially and when made successfully and pioneeringly using it in the rubber vulcanizing art.

In arriving at the conclusion that the prima facies of Weiss' patent has not been met, we deem it proper to say that while we have not discussed, we have not overlooked, the many other matters disclosed in the proofs and argued by counsel. We have only discussed what we regard as its decisive features but we deem it proper to say, without discussing the evidence, we have reached the conclusion that the time date of entry by Weiss in the experiment book was February 10, 1919, as contended by the plaintiff and not September 10, 1919, as contended for the defendant. We deem it proper to say also that we have not discussed the technical contents of the Philadelphia paper for two reasons; first, our technical inability to do so; and second, the needlessness of doing so, had we been able, because for the purposes of this case, we have the evidence of its reader, uncontradicted by his associates, that its purpose was not to disclose a useful, workable process, but on the contrary not to do so.

In reaching the conclusion we have we regret to find ourselves at variance with those reached by two Circuit Judges of the Second Circuit, reported at 292 Fed. Rep. 555, heretofore referred to, but such regrettable divergence of view is lessened by the fact that the views of two other Circuit Judges of that Circuit are in accord with our own.

So holding, the decree entered below will therefore be reversed and before the mandate goes down an opportunity will be given counsel to agree as to its form.

Woolley, Circuit Judge, dissents.

[File endorsement omitted.]

IN UNITED STATES CIRCUIT COURT OF APPEALS

[Title omitted]

Appeal from the District Court of the United States, for the Western District of Pennsylvania

DECREE—Filed December 7, 1926

This cause came on to be heard on the transcript of record from the District Court of the United States, for the Western District of Pennsylvania, and was argued by counsel.

On consideration whereof, it is now here ordered, adjudged, and decreed by this Court that the decree of the said District Court in this cause be, and the same is hereby reversed, with costs.

Philadelphia, December 7, 1926.

Per Curiam:

Buffington, Circuit Judge.

[File endorsement omitted.]

Petition for rehearing, covering 15 pages, filed January 7, 1927, omitted from this print. It was denied and nothing more by order January 26, 1927.

IN UNITED STATES CIRCUIT COURT OF APPEALS

[Title omitted]

ORDER DENYING PETITION FOR REHEARING—Filed January 26, 1927

And now, to wit, January 26, 1927, after due consideration, the petition for rehearing in the above-entitled case is hereby denied.

Philadelphia, —— —, ——.

Per Curiam:

—— ——, Circuit Judge.

[File endorsement omitted.]

Clerk's certificate to foregoing transcript omitted in printing.

SUPREME COURT OF THE UNITED STATES

ORDER ALLOWING CERTIORARI—Filed April 11, 1927

The petition herein for a writ of certiorari to the United States Circuit Court of Appeals for the Third Circuit is granted. And it is further ordered that the duly certified copy of the transcript of the proceedings below which accompanied the petition shall be treated as though filed in response to such writ.

Endorsed on cover: File No. 32,482. U. S. Circuit Court of Appeals, Third Circuit. Term No. 182. Corona Cord Tire Company, petitioner, vs. Dovan Chemical Corporation. Petition for writ of certiorari and exhibit thereto. Filed February 21st, 1927. File No. 32,482.